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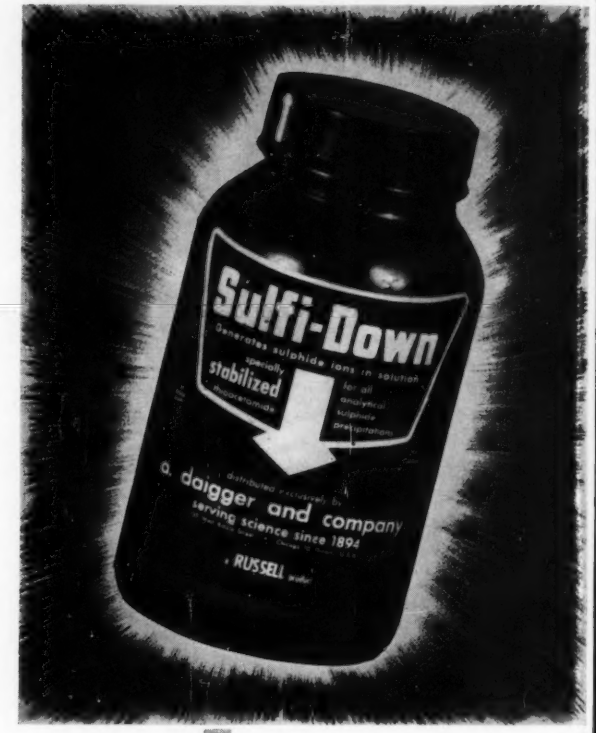

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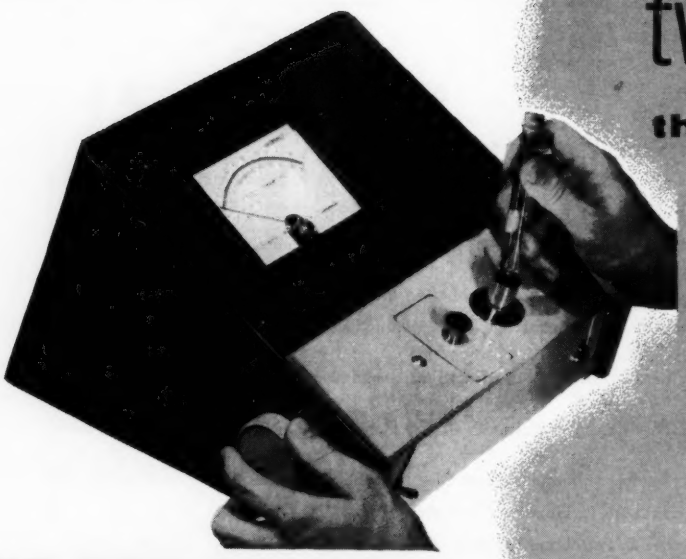

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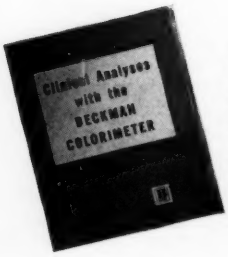

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First series, Sheets 1–24, compiled by HUBERT N. ALYEA, Princeton University, Princeton, New Jersey

Subsequent sheets are to be compiled by the Committee on Tested Lecture Demonstrations, Division of Chemical Education, American Chemical Society, FREDERIC B. DUTTON, Chairman, Michigan State College, East Lansing, Mich.

Journal of CHEMICAL EDUCATION

Instructions for assembling kits for

Tested Demonstrations in General Chemistry

● **Tested demonstrations, monthly publication of which begins with this issue of the Journal, is designed to give the student an opportunity to see some stimulating experiments, and to help the teacher in organizing his demonstration material in a minimum of time. It is recommended that the teacher (1) Purchase the equipment listed on this page, (2) set up the Lecture Desk Equipment described below, and (3) type labels, as listed in the footnotes from month to month, fasten them to the bottles with Scotch Tape, fill them with the chemicals and lay away in the metal cabinet, one or two drawers to each topic.**

EQUIPMENT FOR STORING CHEMICALS

The bottles and jars listed here will contain quantities of chemicals sufficient to perform each experiment four times. If there are several teachers, each should use no more than one-quarter of the contents of each bottle. The following equipment meets requirements for all 24 topics to be described during the coming two years. This equipment is designated by the following:

CODE:

d	a 1 oz. dropping bottle
N	a narrow-neck 4-oz. bottle
w	a wide-mouth $1^1/_2$ oz. bottle
J	a $1^3/_4 \times 5''$ plastic jar
aq	indicates 3-Molar aqueous solutions.

3 gross (432) Number B-5870 Bottles, dropping, screw cap, square, Flint glass, straight glass dropper, removable rubber bulb, and molded Plastic Cap. Capacity 1 oz., approximately $15.12 per gross.

1 gross (144) Number B-5115 Bottle, Narrow mouth, screw neck, French square, Flint Glass, without caps, capacity 4 oz., $7.00.

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Available from Celluplastic Corporation, 50 Avenue L, Newark 5, N. J.

3 (three) number 630 Steelmaster File Cabinets, 30 drawer each, drawer size $3^1/_8 \times 9 \times 15^3/_4''$, overall size $36^1/_2 \times 31 \times 16''$, two partitions each drawer, 180 partitions total, green finish (also comes in grey), approximately $71.50 each. Available from Goldsmith Brothers, 77 Nassau Street, New York 8, N. Y.

Although two metal cabinets are ample for holding all kit material, it is convenient to have extra space for storing exhibit boards, special apparatus, and materials for additional experiments.

LECTURE DESK EQUIPMENT

The following lecture equipment should be stored where readily available, probably in the lecture auditorium itself, since it will be used frequently during the year, and is too bulky to be stored in the metal cabinets.

5	Asbestos 6″ squares
1	Balance
5	Beakers 150, 250, 400, 600, 800, 1000 ml.
2	Beakers 2000 ml.
5	Bunsen Burners
6	Bunsen clamps, small
2	Burettes 25 ml.
1	Burner wing tip
2	Clock glasses, 5 cms.
6	Clock glasses, 10 cms.
	Assorted corks
4	Crystallizing dishes, 10 cms.
6	Deflagrating spoons
6	Demonstration cylinders 12″ high
6	Demonstration cylinders 8″ high
4	Erlenmeyer flasks, 500 ml.
4	Erlenmeyer flasks, 1500 ml.
2	Evaporating dishes, 5 cms.
2	Evaporating dishes, 10 cms.
1	Filter paper, pkg., 11 cms.
1	Filter paper, pkg., 20 cms.
2	Florence flasks, 500 ml.
2	Florence flasks, 1000 ml.
1	Florence flask, 2000 ml.
2	Forceps, pairs
4	Fischer burners
2	Glass jars, 2-liter
	Glass tubing, assorted
5	Graduated cylinders, 10 ml.
5	Graduated cylinders, 100 ml.
2	Graduated pipettes, 10 ml.
1	Hammer
6	Hoffman clamps, large
2	Hoffman screw clamps
1	Kipp generator
	Matches
2	Mortar and pestle
1	Pail, 10 quart
200	Paper cups 1″
200	Paper cups 2″
50	Paper plates 8″ dia.
6	Ring stands
	Rings, assorted
	Rubber stoppers, assorted
	Rubber tubing
1	Separatory funnel, 500 ml.
10	Stirring rods
2	Test tube racks
100	Test tubes 6″
50	Test tubes 8″
20	Test tubes 20 × 2″
2	Thermos bottles
2	Tongs
20	Towels
1	Tray, photographic
2	Tripods
6	U-tubes 6″
2	Volumetric pipettes 10 ml.
1	Washbottle
1	Wolff bottle, 2-neck

SPECIAL OR DANGEROUS CHEMICALS

Store the following in a separate place: iodine, potassium, sodium, stock solutions in $2^1/_2$ liter bottles for filling kit bottles, white phosphorus; tanks of common gases including oxygen, hydrogen, chlorine, nitrogen, carbon dioxide, NH_3, and SO_2; concentrated NH_4OH, and the concentrated acids HNO_3, H_2SO_4, HCl, and HAc.

DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

1. CHEMICAL REACTIONS†

A. CHEMICAL ELEMENTS

*1-1 **Exhibit:** minerals, metals and non-metals, tanks of gases such as O_2, N_2, H_2, CO_2.

*1-2 Sealed tubes of chlorine, of bromine, and of iodine. Vial of iodine. 2-liter Florence flask on hot plate. **Exhibit halogens. Sublime a few flakes of iodine in flask.**

*1-3 Sodium, potassium, filter paper, 100-mm. crystallizing dish, forceps. **Blot oil from bits of Na or K the size of a pea. Throw on water. Use darkened room. CARE: stand 5 ft. away, see footnote.**

B. MIXTURES AND COMPOUNDS

*1-4 Electrolysis of water apparatus. Demonstrate, discussing elements, compounds.

1-5 Sugar, iron filings, CS_2, FeS, $PbAC_2$-aq., HCl aq., filter paper, burner, 3 test tubes, test tube holder. **Demonstrate mixtures of Fe+S of varying amounts. Separate Fe from S with magnet. Dissolve out S by shaking Fe+S mixture with CS_2 showing that thumb which stoppered tube for shaking has yellowish S from evaporation. Heat Fe+S, show a compound is formed by testing with magnet, CS_2, and with HCl plus paper moistened with $PbAc_2$.**

C. PHYSICAL CHANGES

1-6 Paper, stick, moth balls in test tube, burner. **Tear paper; break stick; melt and resolidify the naphthalene.**

D. CHEMICAL CHANGES

Combination. (also, see 1–5)

*1-7 Pop bottle containing 2 vols. H_2 + 1 vol. O_2, burner. **Explode.**

1-8 Mg ribbon, forceps, burner. **Burn, forming MgO and a little Mg_3N_2.**

1-9 Rusty iron bar, Fe filings in shaker, burner. **Exhibit rusty bar, slow oxidation; shake filings in flame, rapid oxidation forming Fe_2O_3.**

Decomposition. (Also, see 1–4)

1-10 Twenty-gram pile of ammonium dichromate on asbestos, burner. **Ignite; makes a small volcano. Show in both lighted and darkened room. Green Cr_2O_3 forms, but do not balance equation.**

1-11 HgO in test tube clamped over burner, splint. **Heat. Hg mirror forms. When very hot, test for O_2 with glowing splint, which bursts into flame. Dark residue (Hg or black allotropic form of HgO?) turns orange again upon cooling.**

Displacement.

1-12 Fe spatula, $CuSO_4$-aq. in 600 ml. beaker. **Deposit copper.**

1-13 Cl-aq., KI-aq., CS_2, cylinder. **Few drops of KI-aq. in cylinder half-full of water. Then add few drops Cl_2-aq. Forms brown iodine by displacement. Add 2-inch layer CS_2, shake. Violet I_2 layer forms.**

1-14 $AgNO_3$-aq., Hg in chamois or cloth bag, 600 ml. beaker. **Bag of Hg hanging in $AgNO_3$ solution grows beautiful silver tree.**

1-15 Zn rod, $PbAC_2$-aq., 600 ml. beaker. **Form lead tree.**

Turn the page for additional demonstrations

* Footnotes

STRENGTH OF SOLUTIONS: **all solutions 3 Molar unless otherwise noted.** In ordinary ionic reactions (as in 1-13 and 1-16) a few drops of the 3 Molar reagent in several hundred ml. of water will be suitable.

1-1 Convenient exhibits are (a) metals and non-metals in their EMF sequence; (b) elements arranged according to their groups in the Periodic Table; (c) minerals classified as oxides, sulfides, carbonates, silicates, etc.

1-2 Do not store iodine in a cabinet unless sealed in a glass tube; in a stoppered vial iodine sublimes and causes corrosion.

1-3 Be at least 5 ft. away from the dish and protect face, since when the piece of K just disappears there is often a sudden spurt and shower of sparks. Store K and Na under kerosene or mineral oil. Store with *Dangerous Chemicals*, not in kit cabinet.

1-4 Make a permanent electrolysis apparatus as follows. An H-shaped generator of 12 mm. tubing 2 ft. long with (a) Pt wire electrodes sealed in bottom legs, (b) stopcocks on top of the two arms, (c) levelling bulb and rubber tubing leading to cross-bar, (d) two round corks painted black and floating inside to mark the level of the liquids, (e) 0.1 M H_2SO_4 for electrolyte (with NaOH there is tendency for foaming). Operate on a 22-volt battery.

1-7 A Pepsi-Cola bottle is suitable; do not use larger. Protect against shattering glass by wrapping it with Scotch Tape. Invert it, full of water, in a water trough. Bubble in 1/3 rd. oxygen and 2/3 rds. hydrogen. Keeping bottle inverted, with a ml. water remaining in the neck to act as a seal, insert rubber stopper. Keeps indefinitely. To ignite, unstopper and immediately hold mouth of bottle to burner flame. CARE. Explain it is a "pop" bottle, that water formed, and then pour out the water used as a seal.

Type the following labels and fasten with Scotch Tape to the containers indicated. (For code, see instructions for assembling kits.) 1-5-*J*-Fe filings, 1-5-*N*-CS_2, 1-5-*w*-FeS, 1-5-*d*-$PbAc_2$ aq., 1-5-*J*-magnet, 1-5-*N*-HCl aq., 1-6-*J*-paper and splints, 1-6-*J*-moth balls, 1-8-*w*-Mg ribbon, 1-9-*J*-iron bar, 1-9-*w* with shaker top-Fe filings, 1-10-*J*-ammonium nitrate, 1-10-*J*-ammonium dichromate, 1-11-*w*-HgO, 1-11-*J*-splint, 1-12-*J*-shiny iron bars, 1-12-*N*-$CuSO_4$ aq., 1-13-*d*-Cl_2 aq., 1-13-*d*-KI aq., 1-13-*N*-CS_2, 1-14-*N*-$AgNO_3$ aq., 1-14-*N*-Hg, 1-14-*J*-chamois bag, 1-15-*J*-Zn rod, 1-15-*d*-$PbAc_2$ aq., 1-16-*d*-$AgNO_3$ aq., 1-16-*d*-HCl aq., 1-17-*N*-KI aq., 1-17-*N*-$HgBr_2$ aq., 1-17-*w*-KI, 1-17-*w*-$HgBr_2$, 1-18-*d*-$Pb(NO_3)_2$ aq., 1-18-*d*-$K_2Cr_2O_7$ aq., 1-18-*J*-Pb shot, 1-19-*J*-candles, 1-19-*J*- soda lime.

†By Hubert N. Alyea, Frick Chemical Laboratory, Princeton, New Jersey

DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

Double Displacement, metathesis, double decomposition.

1-16 $AgNO_3$-aq., dil. HCl, 1-liter beaker. **Mix few drops of each in 800 ml. of water.**

1-17 KI-aq., $HgBr_2$-aq., KI, $HgBr_2$, a 25 × 250 mm. test tube, mortar and pestle. **Grind solids. Mix liquids (test amounts beforehand, since orange ppt. may redissolve).**

E. FUNDAMENTAL LAWS

1-18 Large balance, on one pan a 2-liter Erlenmeyer flask containing a few drops $Pb(NO_3)_2$ in 400 ml. water. Lower a test tube containing $K_2Cr_2O_7$-aq. into flask. Counterbalance with a similar flask containing lead shot on other pan. **Show that tipping mixes the solutions, forming yellow ppt., but no weight change.**

1-19 Candle mounted on a cork having several holes in it, and fitted to the bottom of a lamp chimney so that candle will burn inside chimney; cork stopper at top of chimney leading off to soda-lime U-tube, then to suction. Whole apparatus hanging in large balance, counterbalanced with 600 ml. beaker of lead shot. **Burn candle slowly, drawing combustion products through the soda-lime. Show that as candle disappears the weight of candle + chimney + soda-lime increases due to uptake of oxygen from the air.**

Next month's Tested Demonstrations in General Chemistry

2. OXYGEN

University Museum, Philadelphia

Sumerian Pharmacological Tablet

Left: Obverse. Right: Reverse.

(See page 11)

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Both ends of the motor shaft are equipped with ball bearings properly designed to carry the necessary axial and radial thrusts when the stirrer is operated vertically or at an angle. Lubrication is required very infrequently. The substantial sleeve bearing at the lower end of the shaft, being made of oil-impregnated metal, is permanently lubricated. The control surfaces in the governor are made of materials which show negligible wear even after long service.

The lower end of the shaft carries an adjustable chuck which takes any size shank up to 1/4 inch. The stirrer is supported by means of a 13-mm. rod, 20 cm. long, threaded into the side of the housing. The opposite end of the rod is equipped with a binding post so that the stirrer can serve as a rotating anode in electrolytic work or for grounding the motor housing.

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Editor's Outlook

THE science and philosophy of the ancients were strongly anthropocentric; *we* were the center of everything; the universe revolved around the earth and all God's creation was for the benefit of man. We have since learned better, but the thought which I submit this month is that modern science education is in some danger of falling into the same error.

Applied science—which for all practical purposes is engineering—is quite properly devoted to the end of improving man's material comforts and his standard of living. To many of us, it may appear that there is no higher human ambition; but I, for one, believe that there is. Science has a higher appeal than to man's creature needs.

At most, this only puts into new words the old contrast between technology and pure science, with the usual emphasis upon the complete impersonality of the latter. But we need to be continually reminded of this.

Present-day education is criticized for neglect of the subjects like mathematics, science, languages, and others which require close and vigorous application, and for emphasis upon group projects and activities which are supposed to lead to "social adjustment." Granting that education in the past may have been short on socialization, I have a strong conviction that man's moral, spiritual, and intellectual fiber is better strengthened by the proper relation between himself and the great wonderful universe outside him, than by holding hands and singing songs with his friendly neighbors. Or is my philosophy merely old-fashioned?

For a long time now, the tendency has been to build science curricula around man's daily needs and activities: Unit 1, Man's Food; Unit 2, Man's Shelter and Housing; Unit 3, Communication; Unit 4, Transportation; etc. Can this be because the curriculum makers have been so preoccupied with their little daily rounds that they are oblivious to the many exciting and motivating elements in the phenomena of nature itself? Anyway, I think the emphasis is being put upon the wrong thing. We are again making man's comforts and activities the center of everything, whereas all that he learns should increase his humility. Can this be one of the reasons why we are failing to attract into science the number of students we need? We are now dealing with the *results* of science rather than science itself. Such a "man-centered" curriculum is a poor start for future scientists; it is furthermore a poor contribution to a program of general education.

We are now saying to our students: "See what wonderful things science has given us! We can now travel 1000 miles an hour, through the air; in grandfather's day 20 miles an hour, on the ground, was a good clip." Fine, so what? We have never satisfactorily answered the question why we live in this world, but certainly we do not do so merely to make more vitamins and antibiotics in order to live longer and travel faster. It is better to believe that we do so in order to understand and appreciate our world and all that lives and moves within it. This gives at the same time a *personal* and a *social* motive for our knowledge.

If we make such a belief the motivation of our science education I think we will have something which will attract and survive and will realize the old admonition that man cannot live by bread alone.

THE HISTORY OF COLLOID SCIENCE[1]

In Memory of Wolfgang Ostwald

ERNST A. HAUSER
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THE great philosopher and actual founder of modern physical chemistry, Wilhelm Ostwald (1853–1932), stated in one of his books that one of the most important properties of colloidal substances is that they permit the diffusion of crystalloidal matter without noticeable restriction, while they are more or less impermeable to other colloids. He accepted very early the terminology originated by Thomas Graham and made it clear in several publications why matter present in

Wolfgang Ostwald

the colloidal state cannot be treated from a strictly physicochemical point of view. In a book written in Ostwald's memory by his daughter Grete she refers also to her oldest brother, Wolfgang, saying:

> In 1905, immediately after he had received his Ph.D., he accepted an assistantship offered by Jack Loeb in Berkeley, California. There he made the acquaintance of Dr. (Med.) Martin Fisher who became the best and most trustworthy friend of his life, and the man to whom he dedicated his first scientific book, "The World of Neglected Dimensions." At Berkeley he also found his scientific work for life, namely, the still-to-be proved and strengthened science of colloids.

Up to fairly recently only the term "colloid chemistry" has been used in textbooks, for the listing of classes, and as the name for a specific division of chemical societies. This term should have been already abolished in 1927, however, when Wolfgang Ostwald used the term "colloid science" and explained its meaning in the introduction to the ninth and tenth editions of "The World of Neglected Dimensions": "It is peculiar to find that colleagues in other fields of chemistry frequently hold an opinion against colloid science which the author cannot accept as correct...." (*10*).

Only two other scientists had the courage to state openly in the introductions to their books, "Colloid Systems" (1937) and "Colloidal Phenomena" (1939), respectively, that the term "colloid chemistry" must be abolished and "colloid science" used in its place.

In the author's preface to "Colloid Systems" (*1*) A. Buzagh stated:

> In colloid science it is perhaps more certain than in any other science that we cannot greatly further our knowledge if we forcibly create new theories on the lines of old ones to fit new facts, and become prematurely involved in far-reaching generalizations. Moreover it is evident that new phenomena can only be fully understood if we do not attempt to squeeze them forcibly into the framework of our previous knowledge.
>
> It is a mistake for the physical chemist to doubt that colloid science has justified its existence, to fail to recognize its aims, and to hold the opinion that the classical laws of physical chemistry can be directly applied to colloid phenomena, and that an explanation of these pheneomena is automatically provided by the atomic theory. It is equally a mistake to regard colloid science as completely isolated from pure chemistry and physics and as following only its own special laws.

In the preface to "Colloidal Phenomena" (*4*), Ernst A. Hauser said:

> It required men of courage, convinced by their experimental results, endowed with a keen sense of observation, and capable of sound logical reasoning, to free themselves from conventional viewpoints and establish entirely new lines of thought. . . .
>
> It would be suicidal, scientifically, to abandon further attempts to obtain a more profound knowledge of the happenings in this ultramicrocosmos simply because we cannot always describe and predict reactions in rigid mathematical terms as we have been used to doing in other exact sciences. . .
>
> The science of colloids or the study of colloidal phenomena is a necessary amendment to physicochemistry, a bridge between the study of invisible building units of matter—the actual domain of physicochemical studies—and microscopical dimensions.

It was this trio, Wolfgang Ostwald, Buzagh, and Hauser, who made it clear what colloid science involves and why it cannot be classified simply as chemistry or as a side branch of physical chemistry. More attention must be paid to the fact that any matter will

[1] Presented before the Division of History of Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

exhibit colloidal properties if at least one of its dimensions falls within the colloidal range, and that colloid science therefore involves not only chemistry and physics, but is equally important to such other fields as, for example, geology, mineralogy, medicine, biology, and many other fields of science and technology.

WOLFGANG OSTWALD (1883–1943)

The world owes more to Wolfgang Ostwald than most people realize. He was not only an outstanding scientist but an excellent musician who offered quite a few compositions to the world. It was in all probability his love for music which led him to marry, in his early years, an opera star from Leipzig. He had inherited from his parents an overwhelming desire to help human beings and animals. At the very beginning of the Nazi regime in Germany he offered definite proof of this when he managed to find ways and means for a few friends and former students of Jewish faith to escape Germany before any harm could be done to them. This is an undeniable fact which has been completely disregarded by some German refugees who, late in 1945, published some very distasteful statements about his political affiliations. When Ostwald visited the United States for the last time, in 1938 as guest of honor at the Fifteenth National Colloid Symposium, he said to me that he had come only to pay tribute to the development of colloid science in this country and that he did not want to become involved in any political discussion, because he had no interest in politics. He had joined the National Socialist party only because he wanted to retain his position at the University of Leipzig so that he could assist some of his friends in leaving Germany.

Wolfgang Ostwald founded the Kolloid Gesellschaft and also organized and edited the two leading German journals pertaining to research in colloidal fields—*Kolloid Zeitschrift* and *Kolloidchemische Beihefte*. He retained his positions as editor until his death.

In 1912 he wrote a little pamphlet called "The New Developments of Colloid Chemistry." The foreword contains a statement of special importance: "As far as the author knows, no one has yet tried to do justice to the importance of modern colloid chemistry as a new science, considering at the same time its many scientific and technological applications."

Two years later he published the first edition of the book which is considered his most outstanding contribution to colloid science—"The World of Neglected Dimensions." In the introduction to the ninth and tenth editions (1927) he stated:

> People are still trying to consider colloidal systems as, for example, normal solutions and, in spite of their clear differences, to treat them from the standpoint of the classical theory of molecular dispersed solutions and the classical theory of chemical equilibrium of homogeneous systems. Unfortunately, even close colleagues of mine still give no credit to the property of colloid systems as intermediates between homogeneous and heterogeneous systems.

The scientific world must realize that it owes Wolfgang Ostwald far more than the mere coining of the term "colloid science." His formation of the Kolloid Gesellschaft and the inauguration of the two periodicals drew more attention to this new branch of science than most people in those days felt would ever be possible.

He died from cancer of the liver, suffering terribly, on November 22, 1943. Luckily he was not a witness of the complete destruction of his world-famous library in Leipzig during the war.

We should follow his basic suggestions and make it clear that colloid science is a branch of science which can stand on its own. We must remember that it pertains to the reactivity of surfaces and interfaces, not to chemical composition as such.

ALADAR BUZAGH (1895–)

Dr. Buzagh received his advanced education at the Institute of Technology in Budapest, Hungary, and then at the Universities of Berlin and Leipzig in Germany. He received his doctorate from the University of Budapest in 1920. There he inaugurated the Institute for Colloid Chemistry and Colloid Technology, which he still heads.

Buzagh deserves special credit for having been one of the three who always maintained that colloidal problems deserve a special branch of science. He titled his first book "Kolloidik" only because at the end of the first quarter of this century very few scientists yet agreed with this point of view. A year after the German edition was published it was translated into English and issued under the title, "Colloid Systems" (*1*). In the foreword Wo. Ostwald wrote:

Aladar Buzagh

> All are agreed that the science of colloids now constitutes a new branch not only of physical chemistry but possibly even of chemistry and physics themselves. Some of us are of the opinion that colloid science is, in fact, only a new application of the old classical laws.... This is the sense in which the author of the present book understands the conception of the autonomy of colloid science.

Buzagh then writes, very correctly:

> It is no coincidence, but neither is it to be ascribed to any artificially forced tendency, that "the world of neglected dimensions" has become, in two short decades, "the world of not-to-be-neglected dimensions."
>
> Colloid science today is an enormously extended chapter of physical chemistry, admittedly very rich in specialized laws, and with a well-defined program and object. A knowledge of pure physics and chemistry is necessary to enable us to judge when we are confronted with colloid phenomena for which the classical principles of physical chemistry provide no explanation, and the program of colloid science can only be covered with this knowledge.

Buzagh is not only one of the founders of modern colloid science but also an individual of very special character. He has always been a good friend and advisor to all his students. Besides being an outstanding educator, his most basic contributions to colloid science pertain to studies on adhesion, adsorption, peptization, zeta-potential, and what is known as the "Bodenkörperregel." This law, which he worked out jointly with Ostwald, states that colloidal solubility or peptizability is not independent of the quantity of solute present. The concentration of colloidally dissolved substance either increases continuously with the quantity of solute present, or it shows a maximum for an intermediate quantity of solute.

ERNST A. HAUSER (1896–)

Hauser was born in Vienna, Austria, where he received his bachelor's degree just at the start of World War I. He was immediately called into the army, where he served with the Field Artillery and the Ski Troops. After the war he entered the University of Vienna, where his major field was physical chemistry

Ernst A. Hauser

under Dr. R. Wegscheider; he received the degree of Doctor of Philosophy in 1921. During the academic year 1921–22 he was an assistant in the Department of Physics of the University of Göttingen in Germany. There he made the acquaintance of Dr. Richard Zsigmondy, and undoubtedly owes primarily to him his decision to devote his life to colloid science. He became chemist and later chief chemist of the Colloid Chemistry Laboratory of the Metallgesellschaft, A. G., one of the biggest German chemical companies of the day. He was assigned to carry out basic research in the field of spray drying. A group of Britishers hoped that natural rubber latex could be dried by this German method without, however, losing its redispersibility when placed in water again. Hauser soon discovered the basic difference between natural rubber latex and cow's milk, which could be evaporated to a redispersible dry powder when subjected to the drying treatment. He was sent to Malaya to study natural rubber latex from a colloid-scientific point of view. He solved the problem, and his first book, which was devoted exclusively to the colloid science of natural rubber latex, laid the foundation for the modern latex industry.

P. P. von Weimarn

In 1928 Hauser was invited to accept a nonresident professorship at the Massachusetts Institute of Technology and in 1935 he accepted a permanent position there, now holding the title of professor of colloid science. In 1939 he published his fourth book, "Colloidal Phenomena." This title was chosen because he realized that it would be a mistake to call the book "Colloid Chemistry," but he also realized that at that time far too few would accept the term Wolfgang Ostwald had originally coined—"colloid science."

Hauser takes special interest in educational problems and in his individual students. He has contributed a considerable number of publications pertaining to colloid science and has written a number of books, of which "Silicic Science" is the most recent (*6*).

As has already been stated, it was Wo. Ostwald who originated the term "colloid science." But we owe some of the most basic contributions in this branch of science to three other scientists who, at least in those days, seemingly did not yet fully realize what this branch of science actually implies. The first is the Russian von Weimarn; the other two the Germans Zsigmondy and Freundlich.

P. P. VON WEIMARN (1879–1935)

Von Weimarn, the founder of experimental colloid science, began his career in St. Petersburg, Russia, and spent most of his time from 1905 to 1907 in studying and explaining why colloids and crystalloids cannot be considered as two special worlds but that there exist close connections between them. The results of his work are generally known today as "von Weimarn's law of precipitation." He produced over two hundred inorganic precipitates and was always able to obtain extremely fine crystals, coarse flocks, or jellies depending on the concentration of the reacting substances used. He summarized his findings as follows:

> This permitted me to ascertain that any clearly crystalline substance can be obtained in the form of a typical jelly as well as in the form of different precipitates, which according to their structure can be considered as intermediate stages of the two extreme cases of forms of precipitates. I have so far found no single exception to these purely experimental results.

After he had carried out microscopic and ultramicroscopic studies he amended his previous statement with the following words:

> If we sum up the macroscopic, microscopic, and ultramicroscopic facts, we are forced to the conclusion that any solid substance (element or compound) can be obtained as well in the form of sols (crystalline suspensions) and jellies, as in the form of different kinds of precipitates that differ from each other only by a different size of the crystalline grain.

In summarizing his important experimental contribution he stated:

> The so-called colloidal, amorphous, and crystalloidal states are all universal (possible) properties of matter.... Generally speaking, it follows from these investigations that colloids and crystalloids are by no means two special worlds but that there exist close relations between themselves as well as between them and the gaseous and liquid states of matter.

Long before X-ray methods were applied for the determination of crystal structures, von Weimarn had already demonstrated beyond any question that colloidal particles can also have a lattice structure and that this is not confined to perfectly grown crystals or to any dimensional limitation.

RICHARD ZSIGMONDY (1865–1938)

Some may consider it an ironical fact that Zsigmondy, who was a strong supporter of what is known as the solution theory, was the same man who, by pure logical reasoning and strict adherence to the truth of experimental evidence, was the first to discover experimental means for proving the heterogeneity of colloidal solutions. His greatest contribution to colloid science was the invention of the ultramicroscope. In April, 1900, he perceived the presence of individual particles in solutions of glue, gelatine, gold, silver, etc., by using a microscope with very low magnification but illuminating the liquid preparation from the sides by the use of a reflecting mirror and a collecting lens. Shortly thereafter the Zeiss works in Jena built the first so-called slit-ultramicroscope. When Zsigmondy discussed the first observations he made on colloidal gold solutions he stated:

> I hoped that I might be able to find out the truth by microscopical examination of the cone of light which is clearly visible when colloidal gold solutions are illuminated from only one side, as Michael Faraday had originally observed.... Even if their size was below the limit of microscopic resolvability, if the small particles reflected enough sunlight they would be individually perceptible under the microscope just as were the narrow rays of light, and act to a certain extent as fragments of such light slits.

Those who have had occasion to observe a colloidal gold sol under the ultramicroscope will appreciate the vivid description of the phenomenon given by Zsigmondy himself in a lecture shortly after his epoch-making discovery. After he had pointed out that large gold particles float quietly in the fluid and then sink slowly to the bottom or show only an unimportant Brownian movement, and that by considering colloidal solutions as suspensions one would naturally imagine that the gold particles in these, too, would be as quiet as those in the real suspensions, he added:

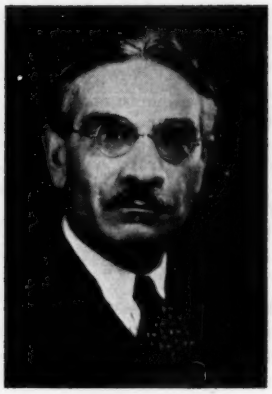
> How entirely erroneous was this idea! The small gold particles no longer float, they move—and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold!... Sluggish and slow in comparison is the analogous Brownian movement of the larger gold particles in the fluid.

Besides being a leading scientist of his years, Zsigmondy always took a great interest in nature. He was also an outstanding teacher and lecturer who took great personal interest in his students and collaborators.

HERBERT M. F. FREUNDLICH (1880–1941)

Freundlich was born in Berlin on January 28, 1880. In February, 1903, he obtained his doctorate from the University of Leipzig with a dissertation on the coagulation of colloid solutions by electrolytes. From 1903 to 1911 he was an assistant in the Leipzig Physico-Chemical Institute, and in 1911 he was elected associate professor of physical chemistry and inorganic technology at the Technische Hochschule at Braun-

Richard Zsigmondy

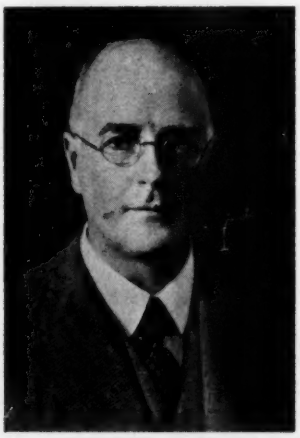


Herbert Freundlich

schweig. Early in 1919 he became chief of the division of colloid chemistry and applied physical chemistry in Professor Haber's Institute in Berlin.

In 1925 the University of Minnesota invited Freundlich to be the guest of honor at the Second National Colloid Symposium. Soon after the National Socialist party came into power in Germany he resigned his position at Berlin and accepted F. G. Donnan's invitation to join University College in London as an honorary research associate. (This was the same college where Thomas Graham, the founder of colloid chemistry, had worked.) In 1937 he was again invited to visit the United States to attend the Fourteenth National Colloid Symposium, which was also held at the University of Minnesota, and the following year he joined the staff of the university as professor of colloid chemistry.

Freundlich, a man of highly cultivated mind, tolerant spirit, and strongly artistic temperament, was always moderate and critical in the statement of his results and he shunned speculative theories. Although he was devoted to research in pure science for its own sake he was always anxious to show the value of applying the results to the explanation and improvement of industrial processes (*2*).



James W. McBain

In 1925 he published, jointly with Hauser, a detailed paper on the colloid chemistry of natural rubber latexes. This paper was the first basic contribution to introduce colloid science into the rubber industry and can therefore be considered as an historical contribution.

Freundlich never used the term "colloid science" because he considered colloid chemistry to be an advanced branch of physical chemistry. When one discussed this problem with him he always referred to "Kapillarchemie" and often said that this term, which he used as the title for one of his books in which every aspect of colloid science was discussed, should actually have been called "Boundary surface chemistry." In the introduction to the first edition of "Kapillarchemie" (*3*) he stated:

> Among the peculiarities of colloid chemistry belongs the fact that the domain may be entered through two doors, so to speak: One may start from a simple system composed of two phases exhibiting a small interface and consider one of the phases as becoming always smaller and more distributed in the other by an increase of the interface.... Or one may start with a true solution, the "molecular dispersed" system, and assume that the size of these particles increases constantly until one enters the field of colloid chemistry. How this increase in size occurs and under what conditions a new phase is formed, as for example by supercooling or supersaturating, is very important for the formation of colloidal systems.

We owe to Freundlich truly basic contributions in nearly every field in which colloid science was active before 1935. One of his greatest contributions was his experimental proof that the Helmholtz double layer theory is not in line with actual facts; he was able to prove the correctness of Gouy's diffuse double layer theory. Another important contribution was his development of a new theory of the electrokinetic "zeta" potential as distinct from the thermodynamic "epsilon" potential, and his work on the problems of thixotropy, rheopexy, and dilatancy.

Freundlich died in Minneapolis of a coronary thrombosis on March 30, 1941, and this event deprived the world of science of one of its most distinguished investigators and expounders of colloid and interfacial phenomena.

The progress of colloid science owes much to other men whose research and teaching in the United States have broadened the scope of this field tremendously. The lives of McBain and Weiser, who are no longer with us, will be discussed in considerable detail. The scientific contributions of Holmes and Reyerson will also be referred to. There are other men who should also be classified as colloid scientists, however. Of these, E. C. Bingham, who died on November 6, 1946, and William D. Harkins, who died on March 7, 1951, at the age of 77, deserve special credit for their many contributions in the field of colloid science, although they called themselves physical chemists. Bingham,

professor of chemistry at Lafayette college, was well known for his studies in rheology, and was considered an authority on fluidity and plasticity, viscosity, and solubility. Harkins was professor of chemistry at the University of Chicago, and at the time of his death was directing important studies in emulsion polymerization, vital to the synthetic rubber program.

JAMES W. McBAIN (1887–1953)

McBain was born in Chatham, New Brunswick, on March 22, 1882. He received his Ph.D. from the University of Heidelberg in 1908. From 1906 to 1919 he lectured on physical chemistry at Bristol, England, and then joined the staff of Stanford University in California in 1926, remaining there until his retirement. With his wife Evelyn McBain, also a famous colloid scientist, he then went to India, where they very successfully established a colloid scientific laboratory.

McBain made many basic contributions to colloid science during his lifetime. The most important is probably his coining of the term "colloidal electrolyte" and his explaining in detail the respects in which it differs from a true electrolyte. He devoted considerable time to the study of the colloidal properties of soaps and similar structures and to work on sorption and adsorption phenomena. Shortly before his death he wrote the book, "Colloid Science" (*8*), in which he offers all his contributions in considerable detail. In the preface he stated:

> This book is designed to give a clear picture of colloid science, bringing out not only its immense scope but also the main regularities and generalizations that have been established within it. Colloid science is a relatively modern subdivision of human knowledge, although its existence was clearly recognized in 1861 by Thomas Graham, who not only first appreciated its importance and generality, but also coined the name "colloid" (from the Greek word for glue) to represent this newly recognized variety of matter.
>
> The approach in this book is that of a physical chemist convinced that the general laws of physics and chemistry prevail throughout this subject, that superimposed upon them are further laws of colloid science, and that all these are operative in living organisms, governing much of their complex and fascinating behavior.

One fact about McBain which has been largely overlooked is that he was a very religious individual. This is best exemplified by his short article in the series, "The Faith of Great Scientists," which was published several years ago. There he said:

> We need personal religion, national religion and international religion. We have been through two wars, with their colossal drama, their high hopes and deep frustrations. We must now betake ourselves to the ensuing task of finding out what to do with a changed world.... Science carries the great ethical message that fearless recognition must be given to truth based on fact finding. It is equally necessary, with science, that there be the "righteousness that exalteth a nation".... Science, whenever it is allowed free expression, affirms the brotherly relationship of all men.

McBain's wife collaborated with him throughout their marriage and she must be referred to as a partner in his work on the formulation of electrokinetics, the constitution of soap solutions and soap films, the structure of jellies, and the electrical properties of soap solutions and their bearing on the electrolytic theory.

HARRY N. HOLMES (1879–)

Holmes, who must be classified as the pioneer of colloid science in the United States, was born on July 10, 1879, and is one of the very few of the older generation who is still with us today. He received his bachelor's degree, majoring in chemistry, at Westminster College and his Ph.D. degree at Johns Hopkins University in 1907. He then joined Earlham College in Richmond, Indiana, where he inaugurated the chemistry department. In 1914 he began his association with Oberlin College, where he constantly pursued a very strenuous program of teaching, research, and administration. I have often heard it

Harry N. Holmes

said that owing to him Oberlin has become the leader in the field of chemical research in the United States as far as liberal-arts colleges are concerned.

Holmes has won many honors and citations and has made basic contributions to colloid science since 1907, including several textbooks. Of special importance is his laboratory manual of colloid chemistry (*7*), his work on silicic acid gels, patents on silica gels of high adsorptive property, and his most recent contributions in the field of biochemical research. For the first six years he was chairman of the National Research Council's Committee on the Chemistry of Colloids and was the editor of Volumes 2 and 3 of the "Colloid Symposium Monographs."

At the spring Meeting of the American Chemical Society in 1954 Holmes was awarded the Kendall Company Award in Colloid Chemistry,[2] an honor he

[2] J. CHEM. EDUC., 31, 600 (1954).

certainly deserves for all his important and basic contributions to colloid science.

HARRY B. WEISER (1887–1950)

Weiser was born in Greencastle, Ohio, in 1887. He received his bachelor's degree in 1911 and his master's in 1912, both at Ohio State University. He then entered Cornell University, where he received his doctorate in 1914. He then went to the University of Tennessee, where he became instructor in chemistry. In September, 1915, he joined The Rice Institute in Houston, Texas, and became professor in 1919. In 1933 he was elected dean of the Institute and held this position until he resigned as active dean on September 1, 1950. He had planned to continue at Rice as professor of chemistry, but died on September 27, 1950.

Weiser wrote six books on colloid chemistry. He was chairman of the National Colloid Symposium of the American Chemical Society for twenty years and editor of the "Colloid Symposium Monograph." He wrote well over one hundred articles on colloid chemistry, all of which were published in the leading chemistry journals of the world.

This is the general information which was offered when Weiser died. In my opinion, however, he deserves far greater recognition than he has received.

Harry B. Weiser

The first work on inorganic colloids was written by him in 1913 ("Indirect analysis of a ferric oxide gel"). Later he made basic contributions to problems of adsorption, electrolysis, adsorption by precipitates, hydrous oxides, on the influence of the concentration of colloids on their precipitates by electrolytes, on the formation of inorganic jellies, on the antagonistic action of ions in the neutralization of sols, on the adsorption and permeability of membranes, on the formation of lyophobic organosols, and on the mechanism of the coagulation of sols by electrolytes; he then devoted considerable time to medical problems, *e. g.*, the rhythmic precipitation in gall stone formation, colloidal phenomena in gall stones, and the synthesis of gall stones; and he made many contributions pertaining to X-ray investigations of inorganic colloids.

In the introduction to the second edition of "A Textbook of Colloid Chemistry" (*12*) Weiser stated:

> A modern physical chemist should know of the heritage left by Nernst and Wilhelm Ostwald even though their classical researches are almost a century old; so too the decades-old contributions of Graham, Wolfgang Ostwald, Freundlich, Einstein, Svedberg, Hardy, Donnan, Perrin, Langmuir, Gortner, and Bancroft should be held up before the present-day student that he may know the solid foundations on which modern colloid chemistry is built and is still growing apace under the inspiring leadership of McBain, Flory, Debye, Williams, Mark, Hauser, and others. The systematic formulation and the critical correlation of the theories of colloidal behavior call for even more wisdom than was needed a decade ago, since the old theories are being put to the test every day and new concepts are being formulated.

I very much doubt that a better proof of Weiser's emphasis on the importance which the history of colloid science deserves can be offered than his own words. From a historical point of view this country owes Harry Weiser above all the inauguration of the colloid symposia and the combined publication of all papers presented at those meetings. To sum up, all of us interested in the advancement of colloid science owe the memory of Harry B. Weiser everlasting gratitude.

LLOYD H. REYERSON (1893–)

Reyerson was born on May 1, 1893, at Dawson, Minnesota. He obtained his A.B. from Carleton College in 1915, his A.M. at the University of Illinois in 1917, and his Ph.D. at Johns Hopkins University in 1920. In 1919 he joined the staff of the University of Minnesota, now holding the position of professor of chemistry; from 1937 to 1945 he was the administrative head of the School of Chemistry there.

During 1927 and 1928 Reyerson was a Fellow of the John Simon Guggenheim Foundation. In 1937 he became secretary of the Division of Colloid Chemistry of the American Chemical Society, and its chairman in 1939. As a member of the A. C. S. he became chairman of the Minnesota Section in 1952 and was elected to the Council Policy Committee in the same year. He was the U. S. delegate to the Internation Union of Pure and Applied Chemistry meetings held in Warsaw in 1927, at The Hague in 1928, and at Stockholm in 1953.

Reyerson is unquestionably one of the outstanding native colloid scientists of the United States. He has published well over one hundred articles; his most important contributions have been the study of adsorption of the halogens, electrokinetic potential measurements, sorption from solutions, magnetic studies of sorbed molecules, detailed studies of colloidally dispersed systems as catalysts, the study of surface oxide systems on active carbons, and particularly the behavior of various forms of carbon, including graphite, toward gases being sorbed on their surfaces.

Besides all this he deserves special credit for the way he organized and managed the Department of Chem-

istry at the University of Minnesota and how he handled his students and worked with them. He now plans to devote himself to pure research, and we can only hope that he will still have many active years in the field of colloid science.

Lloyd H. Reyerson

SUMMARY

The term "colloid science" was originated by Wolfgang Ostwald in 1927. His life and scientific activities are discussed. A. Buzagh and E. A. Hauser joined Ostwald in pointing out that the term "colloid chemistry" was outdated and should be supplanted by the words "colloid science," since this is a field which cannot be considered as merely an appendix to physical chemistry. At about the same time as Ostwald's first contribution to colloid science, the Russian chemist, P. P. von Weimarn, offered the first experimental proof of Ostwald's statements.

The works and lives of Richard Zsigmondy, Herbert Freundlich, James W. McBain, Harry Holmes, Harry Weiser, and L. H. Reyerson are discussed, although most of them did not use the term "colloid science" in their publications.

The work of these scientists offers ample proof that Ostwald's suggestion that we speak of "colloid science" was necessary and valid.

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THE LECTURE DEMONSTRATION OF ATOMIC SPECTRA

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There are numerous methods for demonstrating the spectra of many of the elements. Alyea[1] suggests that the salts of the elements be placed in salt shakers and shaken into an open flame. A more cumbersome method is that given by Frey,[2] which consists of an atomizer arrangement.

A novel and dramatic method for the illustration of this effect was found by the use of so-called "safety fusees,"[3] such as are used by the railroads and highway departments. These fusees can be obtained with red (strontium), green (barium), or yellow (sodium) colored flames and burn with an intense illumination. It was found convenient for lecture demonstration purposes to cut off a one- to two-inch section, place it in a small sand bath, and ignite it with a Bunsen burner.

A section of this length will burn from one to two minutes. The use of this readily available material avoids the necessity and mess of making synthetic mixtures that attempt to show the same effect.

[1] Alyea, H. N., "Student Workbook for Lecture Demonstrations in General Chemistry," privately published, Princeton, N. J., 1950, chap. 20.

[2] Frey, P. R., "College Chemistry," Prentice-Hall, Inc., New York, 1954, p. 53.

[3] Made by the Central Safety Signal Company, Peru, Ind.

A MAILING-TUBE POLARIMETER[1]

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Two flat round corks (Figure 1) are bored. A Polaroid square[2] is placed between them and secured with a strip of plastic tape. Two such units, the polarizer and the analyzer, are constructed. A metal-ended mailing tube[3] is drilled, forming a circular hole at each end. The polarizer is then mounted in the mailing tube with three small nails. The analyzer is likewise mounted. Two strips of white paper are glued about the mailing tube, one on each side of the mailing tube

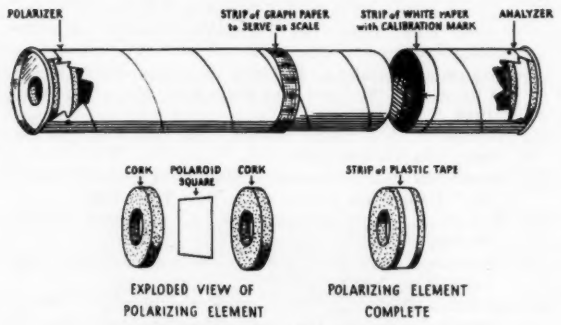

Figure 1. Student Polarimeter

joint. A strip of plastic-sprayed[4] graph paper is then mounted over one of the strips to serve as a scale. The polarimeter tube (Figure 2) is made of a length of glass tubing. Microscope cover glasses are affixed to two drilled rubber stoppers by means of 3M Weatherstrip Cement. One of these stoppers has a small hole drilled just at the edge of the cover glass to permit the escape of air on stoppering the tube.

[1] Presented before the Division of Chemical Education at the Regional Conclave of the American Chemical Society, December 11, 1953, New Orleans, Louisiana.

[2] Polaroid film can be obtained from E. H. Sargent and Company, Dallas, Texas, or the material distributed at "3D" theaters can be used.

[3] Metal-ended mailing tubes 18 in. long and 2½ in. in diameter like those used by the Matheson Company, Joliet, Illinois, for shipping bottled gases, were employed.

[4] The scale and the entire polarimeter were sprayed with transparent plastic from one of the new pressurized dispensers.

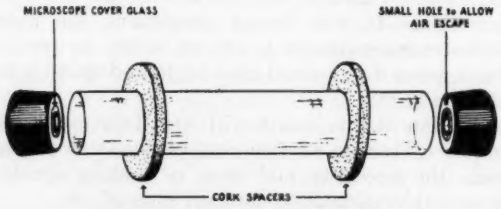

Figure 2. Polarimeter Tube

PROCEDURE

The procedure for conducting measurements with the apparatus is as follows. The polarimeter tube is filled with water and placed in the polarimeter. The instrument is pointed toward a source of light (a window was used), and one end of the mailing tube rotated with respect to the other end until the field turns deep purple. The zero of the instrument is recorded by making a mark on the white paper opposite the zero on the graph paper. Various sugar solutions are then placed in the polarimeter tube and readings are made in terms of the arbitrary graph-paper units. The readings in graph paper units may, of course, be readily converted to degrees by using the conversion factor obtained by determining the circumference of the mailing tube in graph-paper units and equating to 360°.

RESULTS

The extent of optical rotation, α, is proportional to the number of optically active molecules in the light path. The results may be analyzed in terms of the following equation:[5]

$$\alpha = (\alpha)_\lambda^t l(g/v)$$

where l is the length of the path in decimeters, and g is the number of grams of optically active material in v milliliters of solution. $(\alpha)_\lambda^t$ is the specific rotation, a constant for a given temperature, t, and wave length, λ. The equation predicts that a plot of α versus concentration (g/v) will be linear, and such a result was obtained with this instrument.

The polarimeter is used in the physical chemistry laboratory at this institution not only for polarimetry experiments but also in kinetic studies. The quality of the experimental results is somewhat surprising. The excellent agreement of the specific rotation with the accepted value is doubtless somewhat fortuitous.

The cost of materials for the manufacture of the instrument comes to a little under a dollar, in sharp contrast to the cheapest commercial instrument retailing for about four hundred. The chief advantage of the polarimeter, however, lies in the fact that the student can take it apart, and find out for himself exactly how the "magic box" works.

ACKNOWLEDGMENT

The author is indebted to Mr. Thomas L. Keelen for obtaining the experimental results published in this paper.

[5] DANIELS, F., "Outlines of Physical Chemistry," John Wiley & Sons, Inc., New York, 1948.

ANCIENT CHEMICAL TECHNOLOGY IN A SUMERIAN PHARMACOLOGICAL TABLET[1]

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THE chemistry of the ancient Near East, as is true for the beginnings of every basic branch of science, was entirely technological in origin. Because of this, the history of early Mesopotamian chemistry is inextricably intertwined with the development of ancient industries and professions. In the former category, much has been learned from examination of the literature describing such processes as the manufacture of glass[2] and the production of perfumery products[3] from botanical and zoological materials. The third and no less important class of tablet literature bearing on chemical technology includes the works on therapeutics, medical receipts, and pharmacology.

THE OLDEST MEDICAL LITERATURE

A new translation of the oldest medical work known was recently completed by the author in collaboration with Dr. Samuel Kramer, Curator of the Babylonian Section of the University Museum, Philadelphia. The tablet containing this work was unearthed about fifty years ago by an expedition of the museum at Nippur, a site located in the lower part of Iraq, the land of ancient Sumer.

The writing on the tablet is in Sumerian, in a cuneiform script which was performed by means of a wedge-shaped stylus on wet clay. The tablet was then placed in the hot sun to dry or baked in a kiln for preservation. Its date, as determined by its provenience and by the nature of the script, is *ca.* 2100 B.C. Thus it is the earliest known literature in medical annals. In spite of the fact that both Egyptian and Mesopotamian medicine are generally assumed to have had most of their roots in third-millenium B.C. knowledge, until now we have had no direct evidence in the writings of this remote time. For the first time, then, it is possible to move back directly the written technical origin of Babylonian medicine as well as chemistry to this early period, antedating the oldest Egyptian medical papyri.[4]

The tablet (see frontispiece for photographs), measuring 9.5 cm. by 16 cm., is in very good condition on its reverse side and is written in a beautiful hand. The obverse unfortunately has a great number of lacunae and is very difficult to decipher.

TRANSLATION

A part of the Sumerian tablet is given below in translation for discussion purposes. Only those sections are here given which are fairly complete with a reasonable degree of accuracy at this stage of our knowledge of the Sumerian language.

[Lines 96–110] Apportion (?) ... turtle-shell, "horned" alkali (*Salicornia fruticosa* L.), salt, cassia; knead them together with powdered asafetida; wash them in high quality beer [and] boiling water; sprinkle all its solution, its fluid upon it [the ailing organ]; rub tree oil upon it; let pulverized fir-cones be added.

[Lines 111–122] Purify, pulverize the [skin of a] water snake; pour water [over it and over] the *amamashdubkaskal* plant, the root of myrtle, pulverized alkali, barley, powdered fir resin, and [some part of] the *kushippu* bird; boil; let its extract be decanted; wash it [the ailing organ] with the liquid; rub tree oil on it; let *shaki* be added.

[Lines 123–134] Purify, pulverize the ... of a cow; pour water [over it and over] a branch of myrtle, a "star" plant, the root of the *ab* tree [possibly *Commiphora opobalsamum* Engl.], [bark of] the pear (?) tree, [and] *ib* salt; boil; let its liquid be filtered; wash it [the ailing organ] with the filtrate; let potassium nitrate [and] the ... plant be added.

SOURCES OF CHEMICALS

Botanical, zoological, and mineralogical sources were exploited by the Sumerians to derive the drugs found in the text.[5] Mineral substances included are sodium chloride (*mun*), a salt of unknown character (*mun-ib*$_2$) and potassium nitrate (*NE*). Among substances listed from the animal kingdom are milk, (skin of a) water snake, and shell of a turtle.

By far the largest group of chemical materials finds its origin in the botanical kingdom. This includes an interesting variety of plants and trees, some of which were indigenous, while a number of others had to be imported from distant regions. The text implies that many of the botanicals were in a dried state, which would tend to show that they were stored in that condition or had probably been transported after having been dried in a manner analogous to the method of shipment of many botanicals today.

Sumerian medical men used spice (*e. g.*, thyme), cereal (*e. g.*, barley), lupins, trees (*e. g.*, willow, fir, cedar, fig), and a number of plants (*e. g. Mensipermum*,

[1] Presented before the Pennsylvania Association of College Chemistry Teachers at Franklin and Marshall College on March 20, 1954.

[2] THOMPSON, R. C., "On the chemistry of the ancient Assyrians," *Iraq*, **3**, 87–96 (1936).

[3] LEVEY, MARTIN, "Perfumery in ancient Babylonia," J. CHEM. EDUC., **31**, 373 (1954).

[4] SARTON, GEORGE, review of J. H. Breasted's "The Edwin Smith Surgical Papyrus," *Isis*, **15**, 357 (1931).

[5] MEISSNER, B., "Babylonien und Assyrien," Heidelberg, 1920–25, p. 307.

cassia), etc. The botanical drugs were prepared from the seed, gum or gum resin, root, top or twig, wood, and bark. There is also some evidence in the text that the Sumerians carried out oil as well as aqueous extraction. Complete knowledge of these extractive processes has been pointed out in second-millenium B.C. Akkadian tablets describing the manufacture of perfumery products. In this later period the aqueous extracts were obtained at the same time as the extraction of the essential oil was carried out. Cedar oil was a favorite in medical prescriptions, as were aqueous extracts of cedar and cassia.

CHEMICAL TECHNOLOGY

That Sumerian chemical technology was already well advanced in the third-millenium B.C. may be demonstrated from our tablet. The *materia medica* include chemical materials which presuppose a broad acquaintance with many chemical operations, and elaborate procedures are implied in the text in order that the substances listed may have been obtained. To take one example, winning the tree oil from its source would have involved a great number of varied operations, as is evident from the Akkadian perfume literature already mentioned.

Preparation of Simples. There are few directions in our text for the preparation of the simples used in the receipts. It is certain, however, that a sizable body of empirical knowledge had been accumulated in this field. Aqueous and oil extraction have already been mentioned. An infusion of wine or sesame occurs, as well as use of various materials such as asafetida and barley in powdered form. The preparation of the (skin of the) water snake is given as "purify, pulverize," no detailed directions being given. Obviously, this process necessitated a number of operations which are taken for granted in the text.

This is also true in the case of the pulverized alkali (*té-gaz*), which is probably the alkali ash produced by the burning of one of a number of plants of the *Chenopodiceae* rich in soda (most likely the *Salicornia fruticosa* L.). Soda ash derived in this manner was used in the seventh-century B.C. glass texts[6] and also in the much later Middle Ages for glass making. It is of interest that in both cases where alkali is used it is employed together with substances which contain a great amount of natural fats, thus producing soaps to be applied externally on the patient.

Another substance whose winning presupposed further chemical knowledge is potassium nitrate or saltpeter (*NE*). In ancient times the Assyrians probably inspected the surface drains in which such nitrogenous waste products as urine flowed, and when a crystalline formation was found, it was removed for purification.[7] Further problems of separating the components, which included sodium chloride and other salts, were solved by fractional crystallization as the likeliest method. In India and Egypt an old precedure still used is that of mixing lime or old mortar with decomposing nitrogenous organic matter to form calcium nitrate, which is then lixiviated and boiled with wood ash containing potassium carbonate to yield saltpeter on evaporation of the filtrate.[8]

Compounding of Chemical Materials. The general method of compounding is first to pulverize the dry materials in a mortar. This may have been done together with a little liquid, *e. g.*, an aqueous cedar solution. In one instance where the materials are first kneaded,[9] aqueous cassia is probably the liquid used. If the resulting mixture is to be taken internally the pulverized material is mixed with beer. For external applications, the pulverized materials are first boiled in water and then filtered, with the filtrate being retained for use.

In the recipes where the resulting mixture is not to be administered orally, the process of decoction is used. In four of these cases where the reading of the text is fairly certain, not only is boiling water used to extract the sought-for principles but, furthermore, alkali or salts are utilized probably to obtain a greater yield of total extract. Thus we find *Salicornia* and salt, *tè* (probably its ash), *mun-ib*$_2$ (an unknown salt), and salt added, respectively, in these preparations. It is likely that the "salting-out" process was known.

In addition to pulverization, infusion, aqueous and oil extraction, filtration was employed to separate the dregs from the aqueous extract of the decoction. The filtrate contained, in addition to the water-soluble substances, materials in suspension, particularly the highly desirable odoriferous essential oils. Most of the oils were lost, however, owing to their generally low solubility in aqueous solution.

The Sumerian text does not specify the quantities used. The compounder must have known these by heart and purposely excluded them from the written works, possibly in order to shield his secrets from the uninitiated.

SUMERIAN CHEMISTRY AS A SCIENCE

Chemical science has its roots in the accumulation of vast stores of data and techniques. We are indebted to the ancient Near-Eastern peoples for this gathering of empirical facts in chemical technology, which was to be taken up later by the Alexandrian and Muslim chemists.

In context of the Sumerian document which has been discussed, there is no semblance of the magic or mysticism to be found in many of the later Babylonian texts. In fact, if one were to extrapolate our knowledge of the broad rationalism of contemporary Sumerian mathematics, it is obvious that one should expect

[6] THOMPSON, R. C., "A survey of the chemistry of the Assyrians in the seventh century B.C.," *Ambix*, **2**, 3–16 (1938).

[7] THOMPSON, R. C., "Dictionary of Assyrian Chemistry and Geology," Oxford Univ. Press, London, **1936**, p. 7.

[8] PARTINGTON, J. R., "A Textbook of Inorganic Chemistry," Macmillan, London, **1950**, p. 702.

[9] THOMPSON, R. C., "Assyrian prescriptions for diseases of the feet," *J. Roy. Asiatic Soc.*, **1937**, pp. 265–6. (Translation of a seventh-century B.C. text where the drugs are kneaded to produce a plaster for an external application for a foot disease.)

a similar development of an underlying objective philosophy penetrating, more or less, into other fields of ancient Sumerian endeavor. This holds particularly in scientific studies where empirical knowledge is subject to the acid test of a very practical people. From the text alone the evidence remains that the Sumerians possessed a chemical technology without incantations and other supernatural elements. Although a great deal is still unknown of the ancient chemical processes, the text affords an insight into some of their technical knowledge. It is evident that chemistry at the time of our text was well advanced in the accumulation of a body of practical facts. This, of course, was the first important stage leading eventually to the growth of chemical science as we now know it.

ORGANIC FLUORINE CHEMICALS[1]

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At the Chicago meeting of the American Chemical Society in September, 1946, there was a three-day symposium on fluorine chemistry. About 400 people were in attendance at each of the sessions. The March, 1947, issue of *Industrial and Engineering Chemistry* was devoted exclusively to this subject. Since 1946 there has been at least one symposium on fluorine chemistry each year, and now there is a Fluorine Subdivision of the Division of Industrial and Engineering Chemistry. These facts, along with an increasing number of publications in this field, indicate the accelerated interest in fluorine-containing substances.

OCCURRENCE

This paper is concerned with fluorine-containing organic chemicals. However, a brief review of the source of fluorine may be of interest. The most important fluorine-containing mineral, fluorspar (CaF_2), has been used as a metallurgical flux since early times. It was referred to by Basilius Valentinus under the name "fluores" at the end of the fifteenth century. In 1768 Marggraf distilled a mixture of fluorspar and sulfuric acid in a glass retort and obtained a white solid in the distillate. Scheele repeated the experiment in 1771 and pointed out that an acid which he called *Flussäure* was liberated. This was a mixture of hydrofluorosilicic acids. These acids were not differentiated until after the turn of the century (1808) when Gay-Lussac and Thenard carried out the reaction of fluorspar and sulfuric acid in a lead or silver apparatus.

Fluorine in the combined state constitutes a higher percentage of the earth's crust than chlorine. It is the twentieth element in occurrence, existing in approximately three times the amount of copper and fifteen times the amount of lead. Major deposits of fluorspar occur in Illinois; Kentucky; Oklahoma; Derbyshire, England; and South Germany. Another mineral, cryolite (Na_3AlF_6), the most important of the complex fluorides, occurs extensively in Greenland and in lesser amounts in Colorado and the Urals.

HYDROGEN FLUORIDE

Hydrogen fluoride is manufactured on an industrial scale by heating fluorspar with sulfuric acid in a rotating kiln and collecting the gaseous product. The hydrogen fluoride may be purified by distillation and stored in steel cylinders. The disintegration of silicates as in the etching of glass has long been a use for hydrogen fluoride, but its primary uses are fluorination reactions, alkylations, polymerizations, and acylations.

FLUORINE

On June 26, 1886, the French chemist Henri Moissan electrolyzed hydrogen fluoride obtained by distillation from potassium acid fluoride, KHF_2. Later he attempted to demonstrate his experiment to a visiting committee from the Académie des Sciences in Paris, without success. He had redistilled the hydrogen fluoride, whereas in his initial experiment potassium fluoride carried over during distillation had made the liquid a conductor. Moissan carried out the electrolysis in a platinum cell, with platinum-iridium electrodes. Although this discovery is one of the great landmarks in the history of science, the consumption of six grams of platinum per gram of fluorine produced is not very practical.

Fluorine is a pale yellow gas at ordinary temperatures, which condenses to a "canary-colored" liquid at $-188°$ and solidifies at $-218°$. Because of its low

[1] Presented before the North Jersey Section of the American Chemical Society, April 6, 1954, as part of the Passaic Lectures on "Basic Sources of Organic Chemicals."

critical temperature (−129°), it is unlikely that fluorine will ever be transported long distances in large tonnage. It would be more economical to locate a fluorine plant at the site of the commercial application.

During World War II a great deal of work was done on the development of a satisfactory cell. Because of the success of this undertaking, it is estimated that fluorine can now be produced commercially at 0.50 to 0.75 cents per pound, depending upon the scale of production. A practical cell (*1*) has been made with carbon anodes which operates at 2000 amperes, with a current density of 71.5 amperes per square foot, at a temperature of about 100°.

HALOGEN FLUORIDES

Actually, the halogen fluorides, which are readily produced by direct combination of the elements at various temperatures, may be convenient forms for both shipping and using fluorine. For example, chlorine trifluoride boiling at 11.3° can be handled easily as a liquid under a modest pressure, and its reactivity is comparable to that of fluorine itself. On the other hand, others, such as bromine trifluoride, are much less active than fluorine.

METHODS

The foundation for modern organic fluorine chemistry was laid by the brilliant Belgian chemist Swarts during the period 1900 to 1925. It was his work which made the commercial application of aliphatic chlorofluoro compounds as refrigerants possible about 1930. Other pioneer workers in the field were Ruff in Germany, Henne, and then several others in this country. Now there are a variety of excellent methods for introducing fluorine into organic compounds; these may be summarized as follows:

(1) Chlorine, bromine, or iodine in most aliphatic compounds may be substituted by fluorine using (*a*) suitable metal fluorides or (*b*) hydrogen fluoride.

(2) Hydrogen may be substituted by (*a*) certain metal fluorides or (*b*) fluorine.

(3) Fluorine may be added to multiple bonds by means of (*a*) metal fluorides or (*b*) hydrogen fluoride.

(4) The electrolysis of solutions of organic compounds in anhydrous hydrogen fluoride is becoming more and more important in the preparation of a variety of fluorine-containing substances.

(5) The decomposition of aromatic diazonium fluoroborates, the Balz-Schiemann method, is useful for specific fluoro compounds in the aromatic series.

$$C_6H_5N_2Cl \xrightarrow{NaBF_4} C_6H_5N_2BF_4 \xrightarrow{\Delta T} C_6H_5F + N_2 + BF_3 \quad (1)$$

(6) The exchange of hydroxyl by fluoride is a reversible reaction and of only limited interest.

$$HF + ROH \rightleftharpoons RF + H_2O \quad (2)$$

The metal fluorides which are most commonly used in the above methods are:

AgF_2	BiF_5	Hg_2F_2
CoF_3	TlF_3	HgF_2
PbF_4	SbF_5	TlF
MnF_3	SbF_3	CaF_2
CeF_4	AgF	KF

These metal fluorides are used in a variety of ways, and each has its own particular advantage under given conditions.

HALOGEN EXCHANGE WITH METAL FLUORIDES

Antimony trifluoride is a valuable reagent in the fluorination of organic halides having two or more halogen atoms on the same carbon atom. Usually antimony trifluoride is much more effective in the presence of pentavalent antimony halides. This may be accomplished by the addition of small amounts of antimony pentachloride or more usually by the addition of chlorine or bromine to the antimony trifluoride. In compounds like $CCl_3CCl{=}CCl_2$ where the $-CCl_3$ group is allylic, antimony trifluoride converts the trichloro group rapidly and quantitatively into $-CCl_2F$, $-CClF_2$, or $-CF_3$ (*2*). Examples of the use of SbF_3 alone are as follows:

$$C_6H_5{-}CCl_3 \xrightarrow[30°]{SbF_3} C_6H_5{-}CF_3 \quad (3)$$

$$CCl_3CCl{=}CCl_2 \xrightarrow[75°]{SbF_3} CF_3CCl{=}CCl_2 \quad (4)$$

HALOGEN EXCHANGE USING HYDROGEN FLUORIDE

Hydrogen fluoride is a very common fluorinating agent, but it is most useful in the presence of catalysts such as antimony pentahalides. However, it will undergo halogen exchange with very active organic halides such as benzotrichloride. Carbon tetrachloride will react with hydrogen fluoride at 450° and 1000-lb. per square inch pressure to yield CCl_3F and CCl_2F_2 (*3*). In the presence of activated carbon impregnated with ferric chloride, the reaction occurs rapidly at 300° and 100-lb. per square inch pressure to yield primarily CCl_2F_2.

$$CCl_4 + HF \xrightarrow[450°]{1000\text{ p. s. i.}} CCl_2F_2 + CCl_3F + HCl \quad (5)$$

$$CCl_4 + HF/C \xrightarrow[425°]{1000\text{ p. s. i.}} CCl_2F_2 + CCl_3F + HCl \quad (6)$$

$$CCl_4 + HF/(C + FeCl_3) \xrightarrow[300°]{100\text{ p. s. i.}} CCl_2F_2 + CCl_3F + HCl \quad (7)$$

In the manufacture of Freons, the aliphatic chloro compounds are treated with hydrogen fluoride in the presence of antimony trichloride and catalytic amounts of pentavalent antimony halides. Antimony trifluoride and certain pentavalent antimony chlorofluorides are used up in the reaction and regenerated continuously (*4–7*).

$$CCl_4 + 2HF \xrightarrow[SbX_5]{SbF_3} CCl_2F_2 + HCl \quad (8)$$

In some cases, such as in the fluorination of trichloroethylene with HF, antimony pentachloride alone may be used. The latter is fluorinated during the course of the reaction to a mixture of antimony chlorofluorides.

$$CCl_2{=}CHCl + HF \xrightarrow[SbCl_5]{180^\circ} HCl + CClF_2CH_2Cl + CF_3CH_2Cl \quad (9)$$

$$CF_3CCl{=}CCl_2 + HF \xrightarrow[SbCl_5]{250^\circ} HCl + CF_3CHClCClF_2 + CF_3CHClCF_3 \quad (10)$$

SUBSTITUTION OF HYDROGEN BY FLUORINE

Organic compounds have been fluorinated with elemental fluorine since the early work of Moissan. In most instances there have been many products, and the yields of fluorinated compounds having the same number of carbons as the starting material are low. For example, the fluorination of benzene over a copper gauze packing gave eight products (*8*).

$$C_6H_6 + F_2 \xrightarrow[Cu]{90^\circ} CF_4 + C_2F_6 + C_3F_8 + C_4F_{10} + C_5F_{10} + C_6F_{12} + C_6HF_{11} + C_{12}F_{22} \quad (11)$$

With more carefully controlled conditions, particularly temperature, higher yields and less carbon-carbon cleavage occurs (*9*).

$$C_6H_6 + F_2 \xrightarrow[Cu]{265^\circ} C_6F_{12} \quad (12)$$

$$n\text{-}C_7H_{16} + F_2 \xrightarrow[Cu]{135^\circ} C_7F_{16} \quad (13)$$

$$C_6H_4(CF_3)_2 + F_2 \xrightarrow[Cu]{200^\circ} C_8F_{16} \quad (14)$$

SUBSTITUTION OF HYDROGEN BY METAL FLUORIDES

The heat of reaction for the substitution of hydrogen by fluorine, calculated from bond strengths, is −104 kg.-cal. compared with −23 kg.-cal. for chlorination. The values for the additions to the double bond are −107 kg.-cal. and −33 kg.-cal., respectively. The high heat of reaction is overcome partially and concomitantly with less carbon-carbon fission by the use of metal fluorides such as CoF_3 and AgF_2. Using CoF_3, the heat of reaction for the substitution of hydrogen is only −46 kg.-cal.

ADDITION TO MULTIPLE BONDS

Lead tetrafluoride, usually made *in situ* from lead dioxide and hydrogen fluoride, is commonly used for introducing two atoms of fluorine into an olefin (*10*).

$$CCl_2{=}CCl_2 + PbF_4(PbO_2 + HF) \xrightarrow{25^\circ} CCl_2FCCl_2F + PbF_2 \quad (15)$$

Usually this reaction is conducted in an autoclave with the mixture initially at low temperature. The reaction proceeds vigorously when the reactants are allowed to warm to room temperature. Lead trifluoride is also useful at elevated temperatures for replacing chlorine by fluorine in chlorocarbons.

In highly chlorinated olefins it is possible to add fluorine directly without the use of a catalyst (*11*).

$$CFCl{=}CFCl + F_2 \longrightarrow CF_2ClCF_2Cl \quad (16)$$

The utilization of hydrogen fluoride presents the most reasonable source of the monomer vinyl fluoride. Vinyl fluoride is made by the addition of hydrogen fluoride to acetylene at low temperatures in liquid phase, with BF_3 as catalyst and 1,1-difluoroethane as a by-product.

$$HC{\equiv}CH + HF \xrightarrow[\text{low } T]{BF_3} H_2C{=}CHF + CH_3CHF_2 \quad (17)$$

THE ELECTROCHEMICAL PROCESS

One of the important advances in the industrial preparation of fluorine-containing compounds is the electrolytic process (*12*). An organic compound is subjected to electrolysis in anhydrous hydrogen fluoride and, depending upon the conditions, either fluorocarbons or perfluoro organic compounds with functional group intact may be produced. Acids, esters, alcohols, or ethers may be treated to give the fluorocarbon with the same number of carbons as in the original alkyl group. Perfluoro acids, amines, ethers or acid fluorides may be produced by varying the conditions.

$$C_5H_{12} \xrightarrow{HF} C_5F_{12} \quad (18)$$

$$CH_3CH_2CH_2COOH \xrightarrow{HF} \begin{matrix} CF_3CF_2CF_3 \\ CF_3CF_2CF_2\overset{\overset{O}{\|}}{C}{-}F \end{matrix} \longrightarrow CF_3CF_2CF_2COOH + HF \quad (19)$$

The process is carried out in an iron cell using nickel anodes and steel cathodes and voltages between 6.0 and 7.5.

FREONS

The "Freons," developed by Midgley and Henne (*13*), were the first fluorine-containing organic compounds to be used in large tonnages. Swarts (*14*) prepared the first fluorohalomethane, CCl_2F_2 (Freon 12) in 1907. The many methane and ethane derivatives of the "Freon" type have found wide application as solvents, propellants, heat transfer media, and recently as intermediates in the synthesis of other fluorine-containing organic compounds.

POLYMERS

The recent widespread interest in fluorinated plastics has developed subsequent to the "tailor-made" materials prepared on the Manhattan Project. Teflon, Kel-F and Fluorothene have proved most successful commercially, although other types of fluorine-containing polymers are being developed.

$$\underset{\text{Freon 22}}{CHClF_2} \xrightarrow{700°} CF_2{=}CF_2 \xrightarrow[80°]{\text{1000 p. s. i.}} \left[\underset{\text{Teflon}}{CF_2CF_2}\right]_x \quad (20)$$

$$CClF_2CCl_2F + Zn + C_2H_5OH \rightarrow CF_2{=}CFCl \xrightarrow{Bz_2O_2} \left[CF_2CFCl\right]_x \quad (21)$$

Perfluorobutadiene, a potentially useful monomer for homo- and copolymerization, may be prepared by the treatment of hexachlorobutadiene with fluorine in the presence of lead oxide and subsequent dechlorination.

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \xrightarrow[130\text{–}140°]{PbF_4} CClF_2CClFCClFCClF_2$$

$$\xrightarrow{Zn} CF_2{=}CF{-}CF{=}CF_2 \quad (22)$$

The diene may also be prepared by the simultaneous dimerization and fluorination of CFCl=CFCl and subsequent dechlorination (*15*).

Of the polymers, Teflon and Kel-F have received the greatest use because of their water repellency, insolubility, high softening points, good low-temperature characteristics, and resistance to acids and oxidation. Replacement of one fluorine by a chlorine atom improves certain of the working characteristics, but some over-all loss in the electrical and thermal stability is noticed.

Other polymerizable fluorine-containing olefins which have been studied are:

$$CCl_2{=}CH_2 + HF \rightarrow CFCl{=}CH_2 + CF_2{=}CH_2 \quad (23)$$

$$CHF_2CH_2Br \rightarrow CHF{=}CH_2 \leftarrow HF + CH{\equiv}CH \quad (24)$$

The unique physical properties of the various polymers containing fluorine have resulted in their use both as solid materials and as liquids for lubricants, such as liquid Kel-F, Fluorothenes, Fluorolubes and the fluorocarbons.

FLUOROCARBONS

A practical synthesis of the simple fluorocarbons has been noted above. The specific chemical and physical properties of these and cyclic or fused-ring fluorocarbons are of utmost importance, however, and from what has been published, certain generalizations are possible.

A typical synthesis of perfluoronaphthalene (*16*)

$$C_{10}H_8 + 26AgF_2 \rightarrow C_{10}F_{18} + 26AgF + 8HF \quad (25)$$

indicates the general process. In the fused-ring fluorocarbons there is a startling difference between the hydrocarbons and their fluorine analogues.

In a comparison of the boiling points of the chloro- and fluoromethanes, it is of interest to note that after an initial rise to CH_2F_2 the polyfluorinated methanes decrease in boiling point, but the chloro compounds increase. There is also an interesting comparison between fluorocarbons and hydrocarbons. When there are less than four carbons the boiling points of the fluorocarbons are higher than those of the hydrocarbons, but with the pentanes and above the hydrocarbons have the higher boiling points. A comparison of the fused-ring compounds shows that the perfluoro compounds are regularly lower-boiling.

PERFLUORO ACIDS

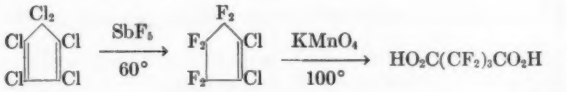
With the commercial utilization of the electrochemical process for fluorination, any even-numbered perfluoro acid is available by proper choice of the acid (*17*). The odd-numbered acids are more difficult to obtain by this process, since the perfluoro acid fluorides appear to decompose.

Trifluoroacetic acid may also be prepared by oxidation of $CF_3CCl{=}CClCF_3$.

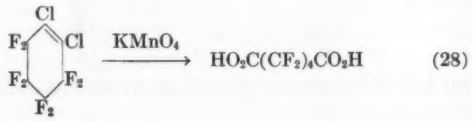
$$CCl_2{=}CClCCl{=}CCl_2 \xrightarrow{SbF_5} CF_3CCl{=}CClCF_3 \xrightarrow{KMnO_4} 2CF_3COOH \quad (26)$$

An elegant synthesis of perfluoro acids has been described by Haszeldine (*18*) in which a perfluoro iodide is telomerized with tetrafluoroethylene. The resulting iodide is added across acetylene and the resulting olefin oxidized to the acid.

The perfluoro dicarboxylic acids may be made by the electrochemical process, but the initial preparation of perfluoroglutaric and adipic acids utilizes the following scheme (*19*).



(80–90%) (27)



(28)

The perfluoroadipic acid has been converted to the diethyl ester; subsequent treatment with lithium aluminum hydride produced the 1,6-glycol in 90 per cent yield. By appropriate syntheses diamides, dinitriles, and diamines have been obtained.

CLAISEN CONDENSATION

Ethyl difluoroacetate does not react with sodium ethoxide. The Claisen condensation can be brought about by the stronger base NaH (*20*).

$$CHF_2CO_2Et + NaH \xrightarrow{70°} CHF_2COCF_2CO_2Et + H_2 \quad (29)$$

Sodium hydride can abstract a proton from the ester, and the formed carbanion reacts with another molecule of ester (*21*).

The hydrolysis of ethyl tetrafluoroacetoacetate with 10 per cent sulfuric acid gives the keto acid. Stronger (40 per cent) sulfuric acid furnishes sym. tetrafluoroacetone in good yield.

$$CHF_2COCF_2CO_2Et + 10\%\ H_2SO_4 \xrightarrow{100^\circ} CHF_2COCF_2CO_2H \quad (30)$$

$$CHF_2COCF_2CO_2Et + 40\%\ H_2SO_4 \xrightarrow{90^\circ} CHF_2COCHF_2 \quad (31)$$

The fluorinated acetones form a series of ketones with boiling points which decrease with increasing fluorine content. 1,1,1-Trifluoroacetone can be brominated in basic or acid medium (*22*).

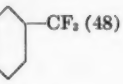
$$CF_3COCH_3 + Br_2 \xrightarrow[CH_3CO_2Na]{CH_3CO_2H} CF_3COCH_2Br + CF_3COCHBr_2 + CF_3COCBr_3 \quad (32)$$

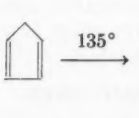
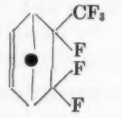
$$CF_3COCH_3 + Br_2 \xrightarrow{\text{con. } H_2SO_4} CF_3COCH_2Br + CF_3COCHBr_2 \quad (33)$$

The carbonyl group in bromotrifluoroacetone can be reduced by lithium aluminum hydride (*22*).

$$4\left(\begin{matrix}CF_3\\ \diagdown\\ \quad C{=}O\\ \diagup\\ CH_2Br\end{matrix}\right) + LiAlH_4 \rightarrow LiAl\left[\begin{matrix}O-\overset{CF_2}{\overset{|}{C}}-H\\ \quad\quad |\\ \quad CH_2Br\end{matrix}\right]_4 \xrightarrow{H_2SO_4} HO-\overset{CF_3}{\overset{|}{C}}-H \quad (34)$$
$$\qquad\qquad\qquad

butadiene, cyclopentadiene, and anthracene.

$$CF_3CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{180^\circ} \text{  } \quad (48)$$

$$CF_3CF{=}CF_2 + \text{  } \xrightarrow{135^\circ} \text{  } \quad (49)$$

FLUORINATED CARBONYL COMPOUNDS REDUCED BY GRIGNARD REAGENTS

Trifluoroacetaldehyde reacts with ethylmagnesium iodide, giving 20 per cent trifluoroethanol and 60 per cent trifluoro-2-butanol. The analogous reaction with pentafluoropropionaldehyde similarly yields the alcohol, pentafluoro-1-propanol, as the main product (*28*). The amount of alcohol is appreciably reduced in the presence of added magnesium bromide.

$$CF_3CHO \xrightarrow[(2)\ H_2O]{(1)\ C_2H_5MgI} CF_3CH_2OH + CF_3CHOHC_2H_5 \quad (50)$$

$$CF_3CF_2CHO \xrightarrow[(2)\ H_2O]{(1)\ C_2H_5MgI} CF_3CF_2CH_2OH + CF_3CF_2CHOHC_2H_5 \quad (51)$$

A proposed mechanism for the reduction reaction involves an initial complex formation between the carbonyl compound and the Grignard reagent, followed by the shift of a beta-hydride ion of the organometallic compound through a six-membered cyclic intermediate to the carbonyl carbon atom. Nonfluorinated carbonyl compounds uniformly exhibit reduced vapor pressure readings in the presence of magnesium bromide. The vapor pressure of fluorinated ketones is not affected by the addition of magnesium bromide, and it is concluded that they do not form complexes with magnesium bromide. The reaction of fluorinated carbonyl compounds must, therefore, take place without an initial complex between carbonyl oxygen and magnesium of the Grignard reagent since $MgBr_2$ is a stronger Lewis acid than RMgX (*29*).

FLUORINATED ALCOHOLS

From the several Grignard reactions (see above) secondary and tertiary alcohols were obtained. In the case of methylheptafluoropropylcarbinol it was found that dehydration would be effected only at elevated temperatures using phosphorus pentoxide.

In the case of the methyltrifluoromethylcarbinol, it was necessary to pyrolyze the acetate at 500° in order to prepare the 3,3,3-trifluoro-1-propene.

$$C_2F_7CHOHCH_3 + P_2O_5 \xrightarrow{200\text{–}250^\circ} C_2F_7CH{=}CH_2 \quad (52)$$

It was found that hydrogen bromide could be added to the fluorinated olefins to give the reverse orientation (*30*).

$$C_2F_7CH{=}CH_2 + HBr \xrightarrow[C]{140^\circ} C_2F_7CH_2CH_2Br \quad (53)$$

GRIGNARD REAGENTS

Normal Grignard reagents are formed by halides in which fluorine substituents are removed one or more carbons from the other halogen. Thus 3,3,3-trifluoropropyl magnesium chloride can be oxygenated and carbonated.

$$CF_3CH_2CH_2MgCl \begin{cases} \xrightarrow{CO_2,\ H^+} CF_3(CH_2)_2CO_2H \\ \xrightarrow{O_2,\ H^+} CF_3CH_2CH_2OH \end{cases} \quad (54)$$

Heptafluoropropyl iodide, which is obtained from iodine and silver heptafluorobutyrate, reacts with magnesium in tetrahydrofuran at −40° (*31*, *32*).

$$C_3F_7COOH + Ag_2O \xrightarrow[H_2O]{100^\circ} C_3F_7COOAg \quad (55)$$

$$C_3F_7COOAg + I_2 \xrightarrow{150^\circ} C_3F_7I + CO_2 \quad (56)$$

$$C_3F_7I + Mg \xrightarrow[C_4H_8O]{-40^\circ} C_3F_7MgI \quad (57)$$

This Grignard reagent reacts with carbonyl compounds by addition at −50° to −30°.

$$C_3F_7MgI + CH_3COCH_3 \xrightarrow[\text{to } +25^\circ]{-30^\circ} C_3F_7C(CH_3)_2OH \quad (58)$$

$$C_3F_7MgI + CF_3CO_2Et \xrightarrow[\text{to } +25^\circ]{-30^\circ} CF_3COC_3F_7 \quad (59)$$

$$C_3F_7MgI + C_3F_7CHO \xrightarrow{-50^\circ} C_3F_7CH(OH)C_3F_7 \quad (60)$$

A better method for the preparation of the Grignard reagent is the exchange reaction between phenylmagnesium bromide and heptafluoropropyl iodide. With carbonyl compounds this reagent gives good yields of alcohols (*33*).

$$C_6H_5MgBr + C_3F_7I \xrightarrow[0\text{–}10^\circ]{\text{ether}} C_3F_7MgBr + C_6H_5I \quad (61)$$

PERFLUOROALKYLLITHIUM

Perfluoropropyllithium is formed by exchange of heptafluoropropyl iodide with methyllithium. It is thermally decomposed at temperatures above −30° and yields heptafluoropropane on treatment with acid.

$$C_3F_7I + CH_3Li \xrightarrow{-74^\circ} CH_3I + C_3F_7Li \quad (62)$$

$$C_3F_7Li + H_2SO_4 \xrightarrow{35^\circ} C_3F_7H \quad (63)$$

$$C_3F_7Li + \text{heat} \xrightarrow{35^\circ} C_3F_6 + LiF \quad (64)$$

Heptafluoropropyllithium reacts with carbonyl compounds at low temperatures to give the corresponding addition compounds (*34*).

$$C_3F_7Li + CH_3CH_2CHO \xrightarrow{-74^\circ} C_3F_7CH(OH)C_2H_5 \quad (65)$$

$$C_3F_7Li + C_3F_7COOEt \xrightarrow{-40^\circ} (C_3F_7)_3COH \quad (66)$$

FLUORINE-CONTAINING SILANES

These compounds have been prepared from heptafluoropentylmagnesium bromide by reaction with ethyl orthosilicate or with silicon tetrachloride (*30*).

$$C_3F_7CH_2CH_2MgBr + Si(OEt)_4 \rightarrow (C_3F_7CH_2CH_2)_4Si + C_3F_7CH_2CH_2Si(OEt)_3 + (C_3F_7CH_2CH_2)_2Si(OEt)_2 \quad (67)$$

Two perfluoroalkylsilanes have been prepared by the reaction of heptafluoropropyllithium with dichlorodiethylsilane.

$$C_3F_7Li + Et_2SiCl_2 \rightarrow (C_3F_7)_2SiEt_2 + C_3F_7SiClEt_2 \quad (68)$$

USES OF FLUORINE-CONTAINING COMPOUNDS

A whole host of uses and applications have been found for fluorine-containing compounds; a few of the general fields are:

Refrigerants	Rodenticides
Coolants	Lubricants
Plastics	Pharmaceuticals
Dyes	Fire extinguishers
Anesthetics	(CF_2Br_2, CF_3Br)

As the fundamental knowledge of the effect of the fluorine atom on both the physical and chemical properties of all types of organic compounds increases, new uses will be found for new compounds and new compounds will be made for specific uses.

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SOUTHERN CALIFORNIA SECTION A. A. P. T.

The Southern California Regional Section of the American Association of Physics Teachers announces its eleventh annual High-school Physics Test, to be given Saturday, May 14, 1955, at El Camino College, Santa Barbara, University of Redlands, San Diego, and elsewhere as in other years. Details may be secured from Professor Thomas N. Wilson, Chairman, Test Committee, El Camino College, El Camino College, California.

The Section will hold its spring meeting at San Diego State College, Saturday, March 12.

DIELECTRIC-CONSTANT APPARATUS FROM WAR SURPLUS

H. BRADFORD THOMPSON and MAX T. ROGERS
Michigan State College, East Lansing, Michigan

THE measurement of electric dipole moments is of considerable value in studying the structures of molecules, and is not an extremely complicated process. A detailed discussion of the theory and the experimental procedures involved is given in Le Fèvre's monograph,[1] "Dipole Moments," and an introductory discussion has been written by Davidson.[2] The most commonly used procedure requires the measurement of the dielectric constants of a series of solutions of the compound in a nonpolar solvent such as benzene. Such measurements have become a part of the physical chemistry laboratory program in many colleges. The use of this type of experiment might be more widespread if equipment for the necessary dielectric-constant measurements were more readily available. A heterodyne-type capacitance measuring circuit for this purpose, suitable for student or research use, may be made by very slight alteration of the BC-221 frequency meter, available on the war-surplus market. No change in the internal circuit is necessary; the conversion and use of the instrument should not require any advanced knowledge of electronics. The device thus obtained has also been used with a flexible metal diaphragm as a differential manometer, and should be useful in other measurements involving small capacitance changes.

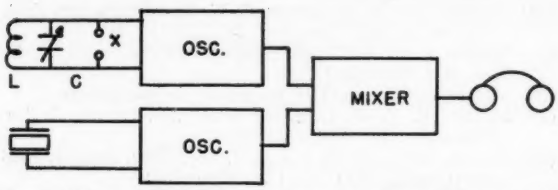

Figure 1. Heterodyne Apparatus for Dielectric-constant Measurements

[1] LE FÈVRE, R. J. W., "Dipole Moments," 2nd. ed., Methuen and Co., Ltd., London, 1948.
[2] DAVIDSON, H. R., J. CHEM. EDUC., 27, 598 (1950).

Figure 2. BC-221 Frequency Meter

THE HETERODYNE METHOD[3]

In the heterodyne method of measuring capacitance changes, widely employed in precise dielectric-constant work on nonconducting liquids, the capacitor to be measured is made part of the tuned circuit of a radio-frequency oscillator, as shown in Figure 1. The frequency, f, of this oscillator depends upon the sizes of the inductance, L, and the total capacitance, C, in this tuned circuit, as indicated by the equation

$$4\pi^2 f^2 LC = 1$$

If the total capacitance, C, consists of the "unknown" capacitor or experimental cell (inserted at X in Figure 1) and a standard variable capacitor, any changes in the cell capacitance may be measured by determining the change in the standard capacitor which is necessary to return the oscillator frequency to its original value.

Accurate reproduction of the original frequency is accomplished by comparing the variable oscillator with a fixed-frequency oscillator, which is generally controlled by a crystal. By means of an electronic "mixer circuit," the heterodyne or "beat" frequency, equal to the difference between the two oscillator frequencies (or between harmonics of those frequencies), is obtained. When the oscillator frequencies (or harmonics) are nearly equal, the beat frequency will be in the audible range, and may be followed with earphones or a loudspeaker. By changing the variable capacitor so as to obtain the lowest possible pitch, the frequency of the variable oscillator may be made to match that of the crystal oscillator.

THE INSTRUMENT

The two radio-frequency oscillators and the mixer in the apparatus described above involve a fair amount of electronic circuitry, and the construction of such an

[3] DANIELS, F., J. H. MATHEWS, J. W. WILLIAMS, ET AL., "Experimental Physical Chemistry," 4th ed., McGraw-Hill Book Co., Inc., New York, 1949, pp. 238–41.

instrument for research purposes can take several months. However, the BC-221 frequency meter, used by the armed forces during the recent war, contains all the circuit components necessary; the only essential change is addition of a connection for a cable leading to the experimental cell. This meter is still available, at prices in the range of $85 to $125, from a number of war-surplus houses.

To make the necessary alterations, the electronic portion of the BC-221 may be removed from the carrying case by loosening the four large screws on the front panel and then pulling the panel forward. The placement of the connector for the experimental cell is shown in Figure 2. A type 83-IR coaxial connector is satisfactory for this purpose, and requires a $^5/_8$-inch hole which must be drilled in the front panel. The center or ungrounded terminal of this connector should be soldered to a short length of insulated wire, the other end of which should in turn be soldered to the stator (stationary portion) of the variable capacitor as shown in Figure 3. This converts the BC-221 to measurement of capacitance.

Though no other changes are necessary, the user may find that certain additional alterations add to the convenience of the instrument. The most important of these is the addition of a line-operated power supply. The BC-221 is normally powered by a 135-volt "B" battery and a set of four 1.5-volt cells providing a 6-volt "A" supply. These batteries are housed in a compartment reached from the back of the case. If the instrument is to be in regular or continuous operation, frequent replacement of the batteries, especially of the 6-volt supply, may be necessary. Substitution of a storage battery for the four 1.5-volt dry cells is possibly the simplest solution to this problem; however, the construction of a line-operated supply may appear desirable. The power requirements of the instrument are 10 milliamperes at 100–150 volts d. c. and 1 ampere at 6.3 volts a. c. or d. c. The circuit shown in Figure 4 is adequate and should cost about $7 to build. The power supply may be easily constructed to fit into the battery compartment of the instrument.

On certain early models of the BC-221 frequency meter a slight change in internal circuitry must be made if an a.-c. 6.3-volt filament supply is to be used. In these models the d.-c. filament voltage was also used to supply the grid-bias potential for one vacuum tube. Whether a change will be necessary for a particular instrument may be determined by studying the circuit diagram found on the inside of the cover of the battery compartment. If the cathode circuit of the final (right-hand) tube in the diagram resembles Figure 5*A* rather than 5*B*, it will be necessary to disconnect the cathode from the filament lead and reconnect it to ground through a 470-ohm resistor. Figures 5*C* and 5*D* show the bottom of the socket for a type 76 tube before and after this change.

Though certainly not necessary, a second change in internal circuitry may prove convenient if a line-operated supply is added. The BC-221 is provided

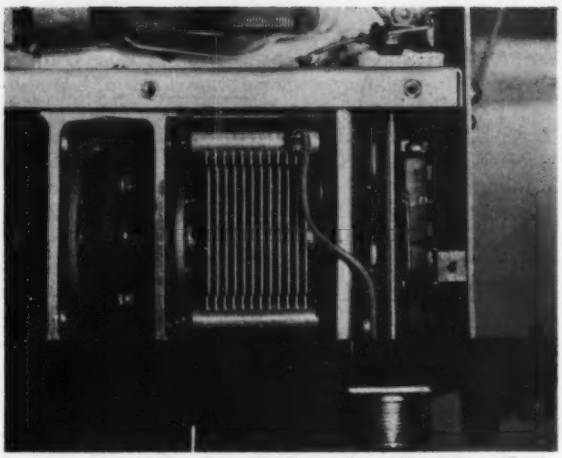

Figure 3. Internal Connection for Conversion of BC-221 for Capacitance Measurement

with an interlock feature on the headphone jack so that when the phones are disconnected the power is turned off. This feature is valuable if the instrument is battery-powered, as the front cover cannot be closed without unplugging the headphones, and the danger of excessive battery drain owing to carelessness is reduced. However, if the instrument is line-operated this interlock feature may become a nuisance, since the instrument operates most satisfactorily when allowed to warm up for an hour or so, and it may not be convenient to leave the headphones connected during this period. Fortunately, the interlock feature is easily removed. By observing the switching action which takes place on the jack when the headphone plug is inserted and removed, one may find the switch terminals providing the interlock and short them with a piece of bare wire.

CELL CONSTRUCTION

The cell for use with this instrument should be of such a size that the highest capacitance to be measured will be within the range of the variable capacitor. The size of this capacitor in the particular model of BC-221 used may be determined from the circuit diagram inside the back cover. As an example, if benzene solutions having dielectric constants of 3 or less were to be examined and the size of the variable capacitor is 140 micromicrofarads, the air capacitance of the cell might well be 30–40 micromicrofarads.

The construction of a glass cell has been described

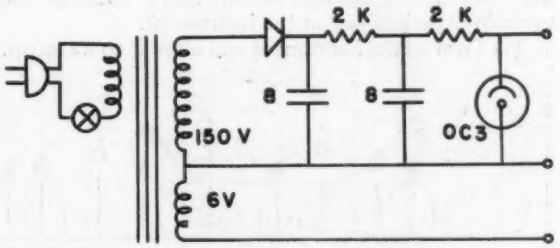

Figure 4. Line-operated Power Supply

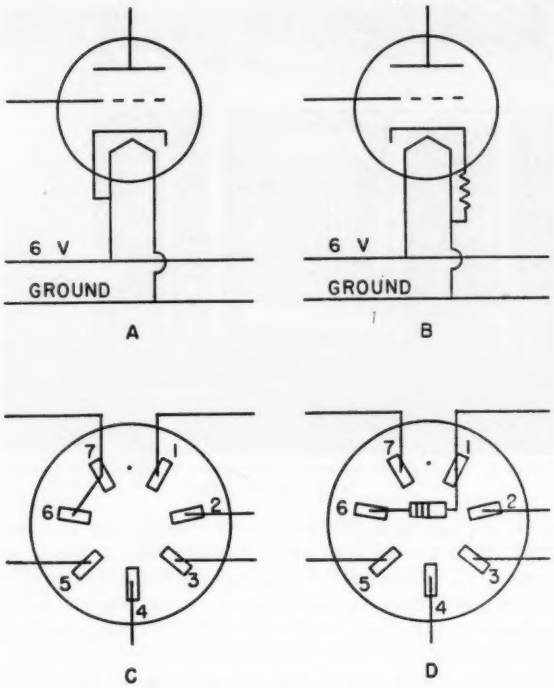

Figure 5. Circuit Changes for Line Operation

by Le Fèvre,[1] and Davidson[2] has described a cell equipped with a water jacket. The authors have recently designed a metal cell with Teflon spacers.

The cell is best connected to the instrument by a coaxial conductor with appropriate connector. The outer conductor or shield should be grounded, and should be connected to the outer cylinder of the cell. In addition, this cable should be as short as possible and should not be moved during a measurement, as the capacitance between inner and outer conductors is included in the apparent capacitance of the cell.

OPERATION

While it is beyond the scope of this paper to describe the entire process of dipole moment determination, stepwise instructions for operation of the instrument and determination of the capacitance change upon introduction of the sample solution to the cell are given below. Before turning on the instrument, the operator should become familiar with the operation of the control with the graduated scale, which controls the variable capacitor within the instrument.

(1) Turn on the instrument and allow it to warm up.

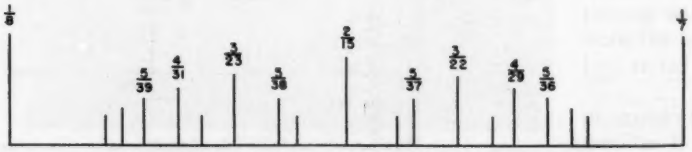

Figure 6. Audible Beat Notes Between 1/8 Megacycle and 1/7 Megacycle

(2) Set the function-selector switch to "Crystal Check" and the range switch to "Low Range."[4]

(3) Connect headphones at the phone jack at the lower left of the control panel.

(4) Connect the empty cell to the instrument.

(5) Set the graduated dial at the upper end of its scale (reading 50.000) and start slowly down scale until a loud, wide beat note is heard. Many different notes will be found as the dial is turned; the one selected for use during the measurement should be loud and broad enough that it may easily be distinguished from its neighbors.

(6) Having found a suitable beat note, adjust the dial carefully until the lowest possible pitch is obtained. If the cell is dry and clean, and if the instrument has been allowed to warm up sufficiently, this pitch will not change with time.

(7) Record the readings of the scales and vernier.

(8) Slowly admit the sample to the cell, noting that the pitch of the audible note changes as the cell is filled.

(9) By adjusting the dial, follow the beat note along the scale until the cell is filled and the note stops moving.

(10) Again find the lowest possible note and record the scale and vernier readings.[5]

(11) After the cell is emptied and cleaned, the next sample may be measured by repeating steps 4 through 10.

CALIBRATION

The two scales of the variable capacitor with the vernier reading provide a total of 50,000 divisions. Unfortunately, this scale does not vary linearly with capacitance, so that a calibration curve must be constructed. Perhaps the simplest method of calibration is to connect a calibrated variable capacitor in place of the cell. The number of points necessary to accomplish the calibration will depend upon the accuracy desired in the results; the calibration curve is fairly smooth, thus simplifying the process.

If desired, the variable capacitor may be calibrated without recourse to any external standard; this procedure depends upon the presence of a hundred or more audible beat notes throughout the range of the instrument. Each of these notes corresponds to a frequency at which some harmonic (multiple) of the variable frequency oscillator is equal to some harmonic of the crystal oscillator, so that the variable oscillator frequency is a rational fraction of the crystal frequency (one megacycle). Starting from the low scale readings

[4] These two controls remain in these positions throughout the measurements; it might even be advisable to remove these two knobs from their shafts to avoid careless changing of the dials and to simplify the appearance of the control panel.

[5] Unless the solutions have been maintained at the measurement temperature, sufficient time must be allowed for the sample to come to the temperature of the bath surrounding the cell before this final reading is made.

and moving "up scale," the strongest and broadest audible signals correspond to $^1/_8$, $^1/_7$, $^1/_6$, $^1/_5$, and $^1/_4$ of one megacycle.[6] From the equation given above, the capacitance at each of these points may be obtained. The weaker signals between these values may in turn be identified. For example, the strongest signal between the ones at "$^1/_8$" and "$^1/_7$" will be at a frequency of $^2/_{15}$ of one megacycle; this will be about midway between the former two. To each side of "$^2/_{15}$" will be "$^3/_{23}$" and "$^3/_{22}$." The strengths of these signals decrease as the numerators of the fractions increase, thus aiding in identification. Signals such as "$^{10}/_{77}$" are clearly audible if this many points are desired for calibration. The "spectrum" of audible beats between "$^1/_8$" and "$^1/_7$" is shown in Figure 6.

This internal calibration cannot be made in terms of conventional capacitance units unless the size of the coil L in the tuned circuit is known. However, if the cell used is calibrated in terms of the arbitrary units selected for the calibration, this will not matter. Measurement of one known capacitance with this apparatus will, of course, permit calibration in terms of micromicrofarads.

As a trial of this apparatus, the dipole moment of 1,2-ethanediol diacetate was determined. The complete procedure for measurement of a dipole moment is beyond the scope of this paper; the method employed has been described by Halverstadt and Kumler.[7] The internal consistency of the data was comparable to that obtained in this laboratory using published heterodyne dielectric-constant circuitry.[8]

Density of the solutions and the refractive index of the pure unknown are also necessary to the calculations; the latter value is often approximated by summing the refractions of the bonds present. In the present case the molar refraction from the measured refractive index was 33.225, while that obtained from bond refractions was 33.216. The dipole moment of 1,2-ethanediol diacetate was found to be 2.82 D.

The instrument may also serve as a differential manometer by observation of the capacitance between a flexible metal diaphragm and a fixed plate. It was thus possible to measure pressures of gases corrosive to mercury and other manometer liquids. An adapted BC-221 is being used in this manner with halogen fluoride vapors.

ACKNOWLEDGMENT

This work was assisted by a grant from the Atomic Energy Commission.

[6] The note at "$^1/_4$" may be off scale at the upper end.

[7] HALVERSTADT, I. F., AND W. D. KUMLER, *J. Am. Chem. Soc.*, 64, 2988 (1942).

[8] CHIEN, J.-Y., J. CHEM. EDUC., 24, 494 (1947).

NOTE ON THE REPRESENTATION OF THE ELECTRONIC STRUCTURES OF ACETYLENE AND BENZENE

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ALTHOUGH the individual π bonds in acetylene have the shape indicated in Figure 11*b* of "A physical picture of covalent bonding and resonance in organic chemistry,"[1] the figure is misleading, since "the superposition of two perpendicular π bonds around the same axis leads to cylindrical symmetry."[2] Hence the accompanying Figure 1 is a better representation of the shape of the electron cloud about the axis of acetylene.

The overlapping of p orbitals in benzene, however, does not lead to a circular distribution as represented by Figure 15*d* of the earlier article,[1] but to a hexagonal shape[3] as illustrated by the accompanying Figure 2.

[1] NOLLER, C. R., J. CHEM. EDUC., 27, 504 (1950).

[2] COULSON, C. A., "Valence," Oxford University Press, Oxford, 1952, p. 193.

[3] COULSON, C. A., N. H. MARCH, AND S. L. ALTMANN, *Proc. Nat. Acad. Sci. U. S.*, 38, 372 (1952); N. H. MARCH, *Acta Cryst.*, 5, 187 (1952).

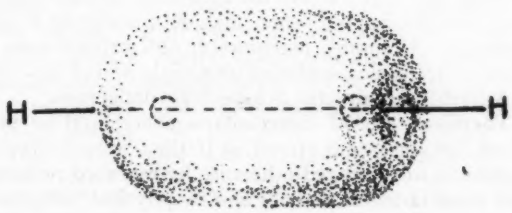

Figure 1

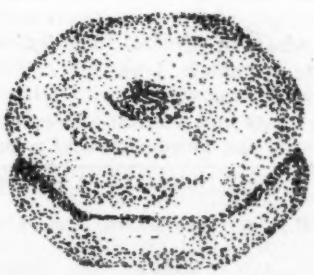

Figure 2

SPONTANEOUS EXPLOSION OF A NORMALLY STABLE COMPLEX SALT

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An impure sample of trihydrazinenickel(II)nitrate was prepared several years ago in this laboratory by the simple method of adding a concentrated hydrazine-hydrate solution to an aqueous nickel-nitrate solution.[1] The product was apparently a mixture of the di- and trihydrazine complexes containing approximately 2.7 moles of hydrazine. The mixture was found to be stable and safe to handle under ordinary conditions, but was fairly sensitive to impact and friction.

Because of this laboratory's interest in extending the range of stable and nonhygroscopic, pyrotechnically active compounds which are sufficiently active to qualify as possible prime flame-producing, initiating, or similar agents, the pure compound was made and studied using the method of Franzen and von Mayer.[2] The method consists of the preparation of the tetramminenickel(II)nitrate as an intermediary with the subsequent replacement of ammonia by hydrazine when the ammine is heated with a hydrazine hydrate solution. The resulting trihydrazinenickel(II)nitrate was a pure salt which was prepared on several occasions by this method in quantities of 5 to 180 grams. On one occasion the moist product produced by this method spontaneously deflagrated. Its drop-weight sensitivity under a 2-kg. weight was 100 per cent at $16^1/_2$ inches, which classifies it as a moderately impact-sensitive compound to be treated with circumspection though with fewer precautions than are reserved for primary explosive mixtures containing such compounds as azides and fulminates.

RECENT WORK

Upon learning of the method of Medard and Barlot,[3] this laboratory produced a small amount of the nickel compound as well as the hydrazine complexes of manganese, zinc, and cadmium as described in the reference. A solution of nickelous nitrate in ethanol was added slowly and with agitation to a 40 per cent solution of hydrazine hydrate in ethanol. The hydrazine was in excess by approximately 5 per cent. The extremely fine pink powder was washed with ethanol and then dried for 16 hours in a vacuum desiccator containing calcium chloride and powdered ethyl cellulose. After drying, approximately 1.5 g. of the product remained in a 120-mm. porcelain evaporating dish.

DESCRIPTION OF ACCIDENT

The dish, containing the powder in the form of a dry cake, was removed from the desiccator and was examined visually without being disturbed. The dish was carried in the person's hand with his index finger extended above it. During this handling, the contents exploded with a deafening report, shattering the dish. About ten minutes had elapsed since the compound had been exposed to the atmosphere. Injuries consisted of a badly bruised finger tip and of a few small scratches on the face. Safety glasses were worn by the victim, this being a requirement for every person engaged in any kind of laboratory work at this installation.

HYPOTHETICAL CAUSES

It appears likely that notwithstanding the thorough washing of the compound on a Büchner funnel, hydrazine was occluded or was present in the form of an unstable higher complex. The presence of filter fibers or of residual alcohol after drying at room temperature is possible. Exposure to air may have initiated a spontaneous decomposition reaction between some uncombined hydrazine and combustible contaminants. These explanations are entirely speculative. However, they agree with similar though less spectacular experiences in this laboratory during the course of synthesis of similar compounds.

RECOMMENDATIONS

Complex salts which contain oxygenated anions of a pyrotechnically active type such as nitrite, nitrate, chlorate, perchlorate, and others in conjunction with a "fuel," such as ammonia, hydrazine, hydroxylammine, organic amines, etc., as a complexing agent are all potential explosives because of the presence of a strong oxidizer and a fuel within the molecule. Some of them are not explosive, but others may detonate more or less violently. Chlorate, perchlorate, and nitrate form a series of decreasing explosive potential; and of the complex-formers, hydrazine is especially dangerous.

Therefore, any of these compounds should be prepared, handled, and stored as if they were initiating explosives until proved otherwise by repeated preparation in an identical manner and by physical tests commonly used for the testing of explosives.

[1] Franzen, H., and O. von Mayer, *Z. anorg. Chem.*, **60**, 247 (1908).
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[3] Medard, L., and J. Barlot, *Chem. Abstracts*, **48**, 6125 (1954).

ARTICULATION OF HIGH-SCHOOL AND COLLEGE CHEMISTRY INSTRUCTION

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OBVIOUSLY, science teachers are motivated by a common interest in science and a desire to pass that interest along to others. To this end, chemistry teachers in both high school and college are responsible for constructive and cooperative efforts. Fortunately, this spirit of cooperation has recently come to the fore. There is far less belittling or lack of appreciation, on the part of the colleges, of the efforts of high-school chemistry instructors than in the 1920's when Kent (*8*) wrote:

> Cooperation is needed between the high schools and colleges. Modern school organization has achieved an acceptable solution to the gap between grades 8 and 9. Having organized curricula for pupils not going to college, the high school now demands that colleges admit all high school graduates. This is inconsistent with school practice below the high school level. Colleges should organize XYZ classes, provide advisors for freshmen, and state their objectives.

Today many colleges do provide for homogeneous grouping when size permits. Student counseling and specific statements as to the objectives of each course are common. In spite of such progress the picture is not all rosy. The already befuddled freshman still frequently hears that frustrating injunction, "Forget your high-school chemistry—this is college!" Is such a charge justified? Is it meant to be taken literally? If the answers to these questions are in the affirmative, it is certainly high time that secondary-school and college chemistry instructors got together more frequently to consider each other's contributions and aims.

An effort in this direction was described in 1954 by Smith (*10*) who recorded some of the suggestions presented in a panel discussing the topic "What the university would like from the high-school teacher." These included, for the future nonphysicist: limited subject matter, applications to everyday living, demonstrations and experiments, and insight into scientific method. For future physicists the suggestions seemed compatible: interest in physics, interest and ability in mathematics, some content, and a little understanding of the nature of research in physics.

A somewhat similar panel discussion was conducted at Cornell University in March of last year. The consensus of several professors of freshman physical-science courses was in line with those mentioned above. Again, interest in the field, adequate mathematics preparation, understanding of a few major principles and techniques, and ability to verbalize were the essentials stressed.

The problem, then, resolves itself into one of vertical articulation. Stripped of the verbosity of an educational dictionary, this term simply implies for our purposes an efficient interrelation of content, method, and objectives between high-school and first-year college chemistry courses. That a problem exists is evident from the frequency of suggestions such as those cited above. It is also evident when one considers the relatively stagnant or even decreasing physical-science enrollment in American high schools.

Johnson (*5*) has reported a decrease of 9.2 per cent in high-school physics enrollment during the period from 1910 to 1949. During the same period, enrollment in high-school chemistry has increased only 0.7 per cent. Meanwhile, biology enrollment has increased 17.3 per cent. Similar statistics for New York State were reported by Van Hooft (*12*) for the period from 1935 to 1953. Physics enrollments again showed slight year-to-year fluctuation but remained fairly constant. Chemistry dropped somewhat during the early 40's then rose again by 1953, but only to 1.2 per cent above the 1935 figure. High-school biology enrollment, on the other hand, doubled during the same period. Could it be that we are keeping youth away from the high-school physical sciences?

Thirty years ago science educators were bemoaning the all too common disregard in college of what the student had done in high school. It is evident that this situation still obtains. During twelve years of secondary-school science teaching, seven of which were devoted almost exclusively to the teaching of chemistry, the author has had several hundred students go on to college chemistry. Not infrequently these students return with the disconcerting report that their professors have advised them to forget their high-school chemistry. Some professors have even suggested that having had high-school chemistry would be a distinct disadvantage to them.

Now what are some of the facts? Are there men of science who are really sincere in this belief or is it a professional ruse designed for such a purpose as that of keeping the former high-school chemistry student on his toes? If they are indeed sincere and their ideas are based on objective evidence, then changes in the high-school chemistry course are mandatory. Whatever their bases, it is appropriate that both high-school science teachers and college professors re-examine their course content, teaching methods, and motives. The literature in this field does not give us the whole answer. No writer seems willing to put the "forget high-school chemistry" injunction into print. However, brief men-

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tion of a few articles dealing with high-school preparation seems appropriate at this point.

In 1936 the Committee on Correlation of High-School with College Chemistry, Division of Chemical Education, published "An Outline of Essentials for a Year of High-School Chemistry" (*7*). Preceding it were suggestions stated somewhat in the form of objectives. A condensation of these is included herein:

(1) To show the service of chemistry to our country
(2) To provide a foundation for college chemistry
(3) To train in observing, exact reasoning, and scientific attitude
(4) To correlate recitation and experiment
(5) To keep laboratory notebooks in concise, clear English
(6) To build on earlier sciences and to interrelate sciences
(7) To encourage use of references and science periodicals
(8) To discover and encourage pupils with scientific aptitude
(9) To stress principles involved in specific cases
(10) To use well-established principles of psychology

Ehret (*3*) of New York University listed in 1948 nine such essentials:

(1) Appreciation of the service of chemistry to our country
(2) Minimum of fundamental topics and principles
(3) Knowledge of scientific method
(4) Ability to express in concise, clear English
(5) High school chemistry should have enabled him to discover aptitude for further study in chemistry—or lack of such aptitude
(6) Easily readable handwriting
(7) Simple arithmetic and elementary algebra
(8) Skill in handling apparatus and materials
(9) Understanding that dishonesty and science do not go together

Rogers (*9*) of Princeton University stressed the necessity for increased emphasis on *understanding* of science, even to the exclusion of some subject-matter content. Better preparation in algebra and laboratory work on a simple scale for all are among his recommendations. Rogers feels that pupils should be "delighted" with their science courses.

Other pertinent comments include a voicing by S. E. Q. Ashley (*2*), of General Electric, of a universal complaint against scientific research workers: namely, their inability to write adequate and understandable memoranda or to spell and write legibly. Gerald Wendt (*13*), Natural Science Department of UNESCO, emphasizes that high school is not the place to train specialists in chemistry. He also mentions, as do others, the need for discovering and encouraging pupils having special science aptitudes.

In still another report, Allen (*1*) mentioned two or three chemistry courses specifically adapted to pupil needs, interests, and abilities. In these, the participating pupils' grade-point averages after one year of college were found to be slightly better than the averages of comparable pupils in more conventional chemistry courses. Williams and Lafferty (*14*), in a study of freshman chemistry students at East Texas State Teachers College, 1948 to 1950, found that a course in chemistry at the secondary-school level appears definitely to be an aid to students who enroll in the beginning course in college.

Two more extensive studies concerning the value of high-school preparation were reported in 1953. One five-year study by Thompson (*11*) showed "a definite correlation between a student's chance of success or failure in general college-chemistry and his previous preparation in chemistry in secondary schools." The other, by Hadley, Scott, and Van Lente (*6*), attempted to demonstrate the value of high-school physics and mathematics as well as chemistry in producing proficient college chemistry students. Trends appeared in their study which supported this hypothesis.

Fully cognizant of the dangers of oversimplification and distortion of meaning, an attempt will here be made to consolidate these suggestions and research findings in order to obtain a clearer view of what attitudes, skills, and knowledge the colleges expect of their entering freshman chemistry students. It is intended that the order in which the following items are listed should reflect the degree of emphasis apparent in the above mentioned references (1—most; 8—least).

(1) Sincere interest in chemistry.
(2) Interest and ability in mathematics (minimum, 2 years in high school).
(3) Understanding of scientific method.
(4) Ability to use clear, concise English.
(5) Minimum of fundamental principles (content).
(6) Legible handwriting and correct spelling.
(7) Understanding of his aptitude or limitations.
(8) Skill in manipulating laboratory apparatus and other materials.

With minor revisions (especially in mathematics) the above list may well be applied to other fields of physical science.

To this point consideration has been given to: (1) the existing situation, both past and present; (2) the necessity for articulation of secondary-school and college chemistry; and (3) a survey of the opinions of selected leaders and investigators in the field. Although considerable space has been devoted to what the college faculty want, little has been mentioned as to what the *students* think is necessary for success in first-year college chemistry.

The writer has recently carried on research involving a random sampling of nearly 1000 freshman science students taking first-year chemistry at Cornell University during the year 1953–54. As a part of this study, questionnaires were answered by these students in which they rated the relative importance of some 56 items involving subject matter, attitudes, and skills in high-school chemistry, physics, and mathematics. They were asked to rate these items either 1 (extremely important), 2 (very important), 3 (moderately important), 4 (insignificant importance), or 5 (uncertain) in terms of adequately preparing high-school students for college chemistry. The percentages of each type of response listed below pertain to a summary of the answers of the first 60 respondents. Final results were not available at the time of writing.

TABLE 1
Relative Importance of Various Factors for Success in First-year College Chemistry

Rank, % "important" responses	*Rank in importance* 1	2	3	4	*Uncertain* 5	*Questionnaire item*
2	37	35	20	3	5	Interest and enjoyment in science
5	22	28	31	17	2	(Av. of responses to 12 mathematics content items)
..	..	..	..	..	..	Understanding of scientific method (not included)
1	40	40	15	5	0	Clarity in expression of ideas
4	32	34	23	7	4	(Av. of responses to 15 chemistry content items)
6	15	13	41	30	1	Neatness in handwriting and spelling accuracy
..	..	..	..	..	..	Understanding aptitude in chemistry (not included)
3	20	25	46	8	0	Individual laboratory work

The first items reported have been selected from the questionnaire and grouped together in Table 1 for comparison of student opinion with the composite opinion of the numerous science educators mentioned previously.

Rated highest in chemistry subject matter were such topics as: gas laws and principles; solution, hydration, and ionization principles; chemical formulas and bonding; equation balancing; atomic and molecular concepts; and chemical mathematics. In the section on high-school mathematics content, exponents and powers of ten and manipulation of decimals were rated highest. In English or other appropriate courses, clarity in expression of ideas, reading for speed and comprehension, and note-taking techniques were most frequently rated important.

A final section of the questionnaire was essentially a rating scale for chemistry teachers. It was designed to obtain student opinion as to the desirable traits of a chemistry teacher. The students' responses are listed in Table 2.

Some general suggestions for improvement of the high-school preparation of future chemistry students were obtained during personal interviews with 110 students from the above-mentioned group. All comments were unsolicited and usually came late in the interview when confidence and rapport was at its peak. The students seemed eager to offer suggestions and frequently expressed the hope that they might be published for consideration by high-school science teachers. A few student recommendations with respect to high-school chemistry follow. No order of importance is implied by this listing.

Separation of college preparatory and noncollege students.
Need to *understand a little* rather than to *memorize much.*
Greater flexibility, but with obvious relationship of topics.
Relate paper-work to actual chemicals and reactions.
More study of theory; less generalization.
Teach oxidation-reduction balancing of equations.
Less stress on industrial and historical chemistry.
More laboratory work (especially quantitative).
Lecture-note-taking techniques.
Greater stress on ionization principles.
More mathematical problem work in chemistry.

With respect to high-school mathematics courses, these students recommended the following:

More scientific problems in mathematics courses, or
A separate physical-science mathematics course.
Many mathematics courses for the college-bound.
More exercises in interpreting and setting up problems.
Use of significant figures.

There are those who insist that college students, especially freshmen, are not qualified to speak on such subjects as course content, necessary prerequisites, or teacher traits. It is interesting to note the parallelism that exists between the opinions of these students and the opinions of the authorities previously cited. The sampling of students used in the above study had a mean score on all examinations during the year within one per cent of the mean score of the 988 students in the total population. This fact plus other similar evidence would seem to indicate that they are representative of the larger group. It does not imply, however, that the results may be considered as typical of freshmen in any college chemistry course.

Returning now to the admonition to forget high-school chemistry, it may or may not be entirely justifiable. The foregoing comments indicate reasons for de-

TABLE 2
Students' Ranking of the Relative Importance of Various Traits in Teachers of Chemistry

% students responding 1, 2, or 3	*Rank in importance* 1	2	3	4	5	*Questionnaire item*
100	57	35	8	0	0	Enthusiasm and interest such that students "catch" it
91	27	32	32	10	0	Definite interest in student study habits
96	36	37	23	2	2	Poise and control of classroom
98	75	15	8	2	0	Mastery of subject
100	93	7	0	0	0	Clarity of explanations
68	2	18	48	28	3	Personal appearance
46	13	13	20	37	17	Tendency to give maximum assignments and tests
85	25	45	15	5	10	Tendency to give moderate assignments and tests
35	10	2	23	50	17	Tendency to give minimum assignments and tests
93	43	28	22	5	2	Pleasant student-instructor relations (both in and out of class)

bating the point either way. The picture is admittedly far from complete, but even the limited facts presented herein spell out the need for further study of this very real problem by those concerned both at the secondary-school and the college levels.

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TESTED DEMONSTRATIONS IN GENERAL CHEMISTRY

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THERE *is* something new under the sun in this issue of THE JOURNAL: the beginning of a monthly page of tested lecture demonstrations in general chemistry. Each issue for the next two years will cover a different topic, 24 in all, so as to encompass the whole area of general chemistry.

Value to the Teacher. Perhaps, as a teacher of general chemistry, you have performed only a few scattered experiments each year because you have not had sufficient time to assemble the materials. If so, this project should help you. For it will enable you easily to prepare material for an entire year's demonstations in general chemistry. You will note that the demonstrations, the first of which series appears in this issue, are marked so that they may be cut out and filed in a loose-leaf notebook as a complete set of lecture experiments.

Topics. The titles for the next two years follow.

A. INTRODUCTION

1. Chemical changes
2. Oxygen
3. Hydrogen
4. Water, acids, bases, salts

B. PHYSICAL CHEMISTRY

5. States of matter, solutions
6. Ionization
7. Energy
8. Equilibrium, oxidation and reduction
9. Atomic chemistry, nuclear reactions, planetary changes

C. CHEMISTRY OF THE ELEMENTS

10. Group 0—the air
11. Metallurgy
12. Group I—alkali metals, copper group
13. Group II—alkaline earth metals, zinc group
14. Group III—aluminum, rare earths
15. Group III–IV—boron, silicon
16. Group IV—inorganic carbon
17. Group V—nitrogen
18. Group V—phosphorus family
19. Group VI—sulfur family
20. Group VII—the halogens
21. Group VIII
22. Other metals—Sn, Pb, Cr, Mn, etc.

D. ORGANIC CHEMISTRY

23. Chain compounds, ring compounds

E. COLLOID CHEMISTRY

24. Colloids

Basic Experiments Only. The first 24 sheets of this series will contain basic experiments only. More spectacular and dramatic experiments may be known, but their use might not be as good pedagogy. For example, the orthodox experiment on elements, mixtures, and compounds involves a series of tests with iron, sulfur, and iron sulfide; using CS_2 to dissolve the S, a magnet to separate the Fe, and HCl and either lead-acetate paper or odor to confirm the sulfide. Now iron, sulfur, and rotten-egg smell are familar to the beginning student,

and it is therefore good pedagogy to use them in an early lecture. A far more bizarre experiment using antimony, iodine, and antimony iodide involves brilliant color changes. But these chemicals are unfamiliar to the beginner, and hence are less valuable pedagogically. Therefore iron-sulfur not antimony-iodine appear in this first series.

Later Series: Tested Demonstrations. However, it is planned, after the first 24 sheets have appeared, to continue the series with more dramatic ways of carrying out these and other experiments. To this end chemistry teachers are urged to submit their favorite experiments to Professor Frederic B. Dutton, Department of Chemistry, Michigan State College, East Lansing, Michigan, who will act as editor for this series, receive your suggestions, and submit them to a panel of teachers for testing in the laboratory. Those demonstrations having special merit will be published later on, with proper acknowledgement to the authors. The demonstrations appearing in this first set of 24 topics have already been tested by the author well over half a hundred times.

Terse Instructions. The teacher will find the instructions very brief. The equipment is listed; then in boldfaced type is stated what the lecturer does, or what occurs. The instructions are sufficient, however, for certainly a teacher knows what to do if he reads:

1-15 Zn rod, $PbAc_2$-aq., 600-ml. beaker. **Form lead tree.**

This will be the fifteenth experiment under Topic 1. The *aq.* is used throughout the series to designate an aqueous solution of 3-*M* concentration. The experiment is to immerse a zinc rod in a 3-*M* aqueous solution of lead acetate. A beautiful dendritic form of metallic lead forms on the rod. In some experiments footnotes amplify the instructions.

Demonstration Kits. Also in the footnotes are indicated labels for the teacher to type, fasten to suitable containers, and lay away in kits, so that the set of experiments can be repeated several times in one year, and from year to year. Details for making these kits are given in the instructions for Topic 1.

Student Workbook. The author has used these sheets in another way. When he lectures on oxygen, for example, he distributes a copy of the oxygen demonstration sheet (Topic 2) to each student. At one point in the lecture he may announce that he is performing experiment 2-9. After performing it, he tells the student to write down on the sheet the equation for what occurred and the principle being illustrated, pausing long enough in his lecture for the student to do this. This forces the student to think rather than to bask idly in the pleasure of the excitement of the experiment. The sheets, collected at the end of the lecture, show the lecturer whether his demonstration was properly understood by the class.

DEMONSTRATION HINTS

Teachers are in the greatest selling game in the world—the selling of intellectual curiosity to their students. Some miscellaneous selling tricks are therefore not amiss at this point.

Lecture Box. A brightly-illuminated lecture box is a prerequisite. An improvement over the box described in THIS JOURNAL (**25**, 249 (1948)) is a single box 12 in. wide × 10 in. high × 8 in. deep, with a backboard 12 × 7 in. and a gooseneck pipe holding a 150-watt spotlight 18 in. above the platform. Two similar boxes without lights are also useful for occasional experiments, one painted white for colored precipitates and one black for white precipitates.

Special Apparatus. Avoid elaborate pieces of apparatus; do not get out a cannon to shoot a fly. Special apparatus which is ready for instant use is preferable to something which has to be laboriously assembled; for instance, build an electrolysis-of-water apparatus with a self-contained battery. Keep the equipment simple. Elegant as a magnetic stirrer is, for example, the sight of the lecturer stirring the solution with a glass rod is more instructive. Often special precautions, such as unnecessary drying of gases by passing through calcium chloride, are extraneous operations which obscure the main reaction and only confuse the student.

Manipulative Techniques. Do not obstruct the view of your apparatus; keep your hands out of the way as much as possible. Arrange the equipment and chemicals in the same sequence as you intend to use them, instead of conducting a frantic search during the lecture. If an experiment fails, do not labor to make it work, desperately repeating it over and over again until the class feels as desperate as you. Instead, relate why you think the experiment failed and promise to carry it out successfully the next day. See that you do. Experiments which fail reflect badly upon the lecturer's ability, or upon his judgment in keeping them in his repertoire.

Surprise, humour, and *truth* are the servants of a good lecturer. Surprise is indispensable; employ it where you can. Let us take the case of mixing 90 ml. ethanol with 10 ml. saturated calcium acetate; a gel forms. The worst way to perform this is to announce that the gel will form, and then mix and stir the solutions until your prediction is fulfilled. Instead, slowly pour alcohol from beaker 1 into the calcium acetate solution in beaker 2; then pretend to pour the mixture back into beaker 1. Since a gel has formed, nothing pours out, much to the astonishment of the class. Then explain what has occurred. Humor is a lifeline in any lecture, especially when anything goes wrong. And truth, nothing but the whole truth, will answer. Never fake experiments. If the experiment is so poor that it needs to be faked, abandon it; instead *turn in this issue to the page of tested experiments which always work!*

RECENT ADVANCES IN PETROLEUM REFINING[1]

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Standard Oil Company (Indiana), Whiting, Indiana

REFINING of petroleum consists of making it into gasoline, heavier fuels, lubricants, and many other products. Gasolines and solvent naphthas roughly comprise the lower-boiling half of all refined petroleum. Heavier fuels for heating and diesel engines make up about one-quarter. Lubricants of many kinds represent nearly one-eighth. Lesser products like chemicals, waxes, asphalts, and coke together make up a little over one-sixteenth. Most of the remaining sixteenth is burned in the refinery to provide the energy needed to process the rest.

Thus, more than three-fourths of petroleum goes into fuels that are burned. Gasoline burns under exacting conditions and deserves by far the most research—fundamental as well as applied. The heavier fuels, burned in devices that are less demanding, require less attention. Naturally, the advances in petroleum refining since World War II, like those of the decade before, emphasize gasoline (*23*). Products other than fuels have also been improved; recent advances in the fields of lubricants and petrochemicals are reviewed elsewhere (*5, 6*).

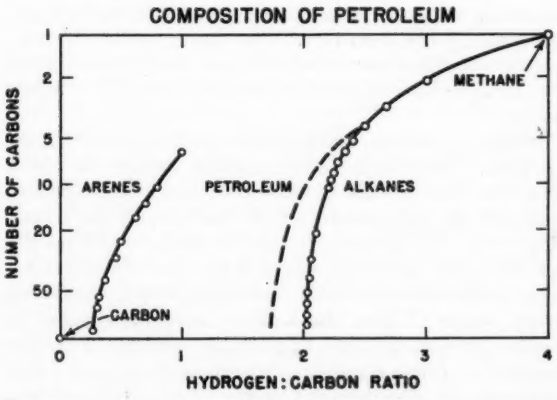

Figure 1

The first job of a refinery is to separate petroleum physically into a series of streams. Some closely resemble the final products, but others must next be converted by chemical change to reach the desired properties. Lastly, individual or combined streams are finished to meet the needs of consumers. These three steps—separation, conversion, and finishing—present a convenient framework for discussing recent advances in petroleum refining.

SEPARATION

Physical processes that separate petroleum usually involve two phases. One is always the liquid phase. In distillation, the other is vapor; in extraction, it is liquid; and in crystallization, it is solid. Many variations of these processes are possible, and all have been improved and extended in recent years. One separation process that does not involve two phases is thermal diffusion; it has not yet been introduced into refineries, although pilot plants are running in several laboratories.

Yesterday's research on composition of petroleum has led to today's refinery separations. Today's composition studies forecast separations that will be used tomorrow (*18*). A fundamental picture of petroleum therefore helps to illustrate practical separation methods. Figure 1 gives such a picture. At left the number of carbons is plotted; because there are fewer hydrocarbons of each successive carbon number in petroleum, the scale is logarithmic. Along the bottom is plotted hydrogen-to-carbon ratio. In the upper-right corner is methane with one carbon and four hydrogens. Downward from the methane corner extend the alkanes toward a ratio of two. For all practical purposes, carbon can be considered to lie in the lower left corner. The condensed polycyclic aromatic hydrocarbons, or condensed arenes, extend upward from near the carbon corner toward a ratio of one.

Petroleum has an average composition that is much nearer the alkanes than the arenes. Distillation separates it vertically by carbon number, and extraction separates it horizontally by H:C ratio. Crystallization and thermal diffusion separate it in a different way that involves the shape rather than size or composition of the molecules.

Distillation

By far the oldest and most common separation process is distillation. Although laboratory fractionation columns have taken many forms in the past 25 years, refinery fractionating towers are only beginning to depart from the bubble-tray design. One reason is that towers don't wear out; if they outlive one use,

[1] Presented at a joint Symposium on "Recent Advances in Petroleum Chemistry" before the Divisions of Chemical Education and Petroleum Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

they are often put to another. The huge 100-tray towers built for the aviation gasoline and synthetic rubber plants of World War II represented the ultimate in bubble trays. Simpler trays and efficient packings are being introduced (*14*). Greater capacity and better separations result; the towers are smaller and cost less.

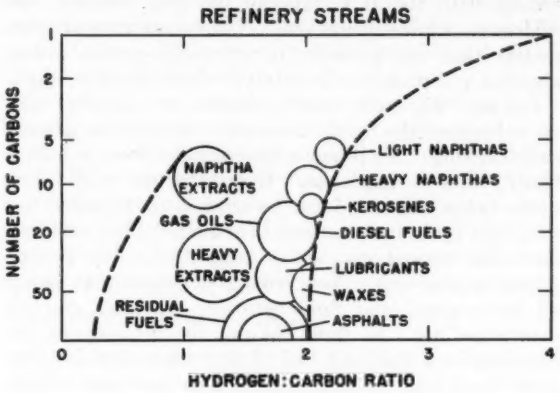

Figure 2

Separation by distillation in refineries has slowly but steadily become sharper. Better packings and more trays eliminate bothersome "heads" and "tails" and increase quality or yield of desired products. Vacuum-distillation units have become standard equipment in the 50 refineries that make lubricating oils.

Extraction

Extraction occurs when a petroleum fraction is mixed with a substance in which it is incompletely soluble. Most substances extract hydrocarbons with the lowest H:C ratio but some do so far more efficiently than others. When the ratio is far apart, as in alkanes and arenes, separation is easy. Arenes are extracted from naphthas because they are desired as chemicals, and from higher-boiling fractions because they are undesirable in lubricants. Compounds that contain oxygen, sulfur, and nitrogen are more soluble than hydrocarbons and accompany the arenes into the extract. Some solvents extract arenes by purely physical action; others form loose chemical complexes with them.

A physical solvent that has come into use recently is diethylene glycol. In the Udex process for removing arenes from naphthas, its solubility is regulated by the addition of controlled amounts of water (*20*). The search for new solvents for heavier fractions continues; exotic solvents have received attention but have not replaced sulfur dioxide and other conventional solvents.

One solvent that acts through complex formation is liquid hydrogen fluoride (*13*). Unlike sulfuric acid, which it somewhat resembles in behavior, it can be recovered by distillation. It has not yet been used commercially because of the high cost of the corrosion-resistant materials needed. When a combination of boron fluoride and hydrogen fluoride is used, the complexes formed with arenes and sulfur compounds are apparently salts of the nonexistent acid HBF_4 (*12*). Extraction is consequently more efficient than with the physical solvents.

Adsorption, long used for decolorizing paraffin wax, somewhat resembles extraction. In the Arosorb process recently developed, arenes are separated from naphthas by silica gel (*9*). Arenes adsorb on the gel more tightly than the alkanes; by flushing successively with butane and toluene, the alkanes are removed and the arenes are recovered.

Crystallization

Dewaxing of lubrication oils is the classical example of crystallization in petroleum refining. The products are paraffin wax, which consists of *n*-alkanes, and microcrystalline wax, which may contain a branch or a ring. Crystallization methods have recently been applied to other hydrocarbons: naphthalene, paraxylene, and cyclohexane are now separated from petroleum streams by crystallization.

An exciting discovery of the past decade was the urea-*n*-alkyls. The ability of urea to form insoluble crystalline complexes with straight-chain hydrocarbons has been thoroughly studied and may soon be used in refineries (*24*). Treatment of fuels with urea separates waxes that cannot be removed in any other way. A deterrent to use in refining has been the large amount of urea required.

Through these separations, petroleum is prepared for conversion and finishing. Figure 2 shows, on the same scale and with the same alkane and arene lines as before, the major streams produced. Distillation has sorted out successively higher-boiling naphthas, kerosene, gas oil, lubricants, and residues. Extraction has removed hydrocarbons with a low H:C ratio and nonhydrocarbons from the naphtha and lubricant fractions. Also from the latter, crystallization has separated wax. But there is more gas oil than is needed for heating homes and for diesel fuel and not enough naphtha for gasoline. And everything except the residues will need further treatment before sale.

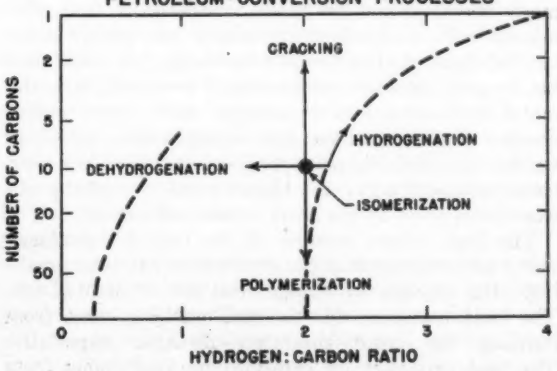

Figure 3

CONVERSION

The earliest conversion process, cracking of gas oil to naphtha, is still by far the most important; the major reaction is breaking of carbon-carbon bonds. Conversions introduced recently, aimed at raising octane number, often involve carbon-hydrogen bonds. A convenient way of classing conversions again makes use of a plot of carbon number and H:C ratio, and is shown in Figure 3. Cracking and polymerization change the size of hydrocarbons with little effect upon H:C ratio and are analogous to distillation. Hydrogenation and dehydrogenation change the ratio but not the size and are analogous to extraction. Isomerization changes neither. A 10-carbon fraction might be converted in any of four directions, although it could not be hydrogenated far without falling in carbon number.

Conversions Affecting Carbon Number

All changing of carbon number was formerly done with heat alone. As the demand for gasoline had increased, larger and larger thermal-cracking units had been built to replace hundreds of small ones. Many large units are still in operation but almost no new ones have been built in the past decade. Better yields of naphtha result from catalytic processes, but even these break more carbon-carbon bonds than necessary. This difficulty is overcome by other processes in which the major reaction is creating carbon-carbon bonds. Together, conversions in the two directions have increased several fold the yield of naphtha produced from petroleum.

Catalytic Cracking. Conversion of gas oil to naphtha over silica-alumina catalysts is now widely practiced. Completely continuous moving-bed and fluidized catalytic-cracking processes have gained favor until the number of units now exceeds 100 and about 30 per cent of all petroleum passes through them. Because efficient fluid units for small refineries are available, the number will perhaps soon approach 200. Eventually almost 50 per cent of petroleum will be processed in them.

Catalysts of satisfactory activity can be made in many ways. Some are made synthetically from aluminum salts and silicates; others are simply acid-treated clays or even blast-furnace slag. A brisk market in used catalysts exists today; some refineries demand fresh and active catalyst and others prefer cheaper discard catalyst that is less active but more stable. A synthetic silica-magnesia catalyst has been tested commercially; the higher yield of naphtha obtained was offset by the lower octane number (*4*).

The high octane number of the naphtha produced was a major factor in the acceptance of catalytic cracking. But another advantage must also be pointed out. The heat necessary for thermal cracking came from burning the gases produced—methane especially. The heat necessary for catalytic cracking comes from burning the coke that is formed on the catalyst. Replacement of the thermal by the catalytic process has shifted cracking from a hydrogen consumer to a carbon consumer.

Although a thoroughly developed process, catalytic cracking still has problems. The capacity of refinery units is limited by the rate at which the coke can be burned (*11*). Because the amount of coke formed increases with the H:C ratio of the feed, extracts are seldom catalytically cracked. The vanadium and other metals that are present in petroleum poison silica-alumina and prohibit the catalytic cracking of residues.

Coking. Extracts and residues are usually converted to naphtha by the destructive-distillation process called coking. To refiners the coking process is both a benefit and a headache. Even streams with H:C ratios below about 1.5 can be cracked to naphtha, but semisolid hydrocarbons remain behind. They accumulate easily enough as coke in large drums, but getting it out is laborious. New coking processes that parallel moving-bed and fluid catalytic cracking simplify coke handling. In fluid coking, the oil streams decompose in a fluidized bed of fine coke particles that grow until they reach about 0.1 mm. and are continuously withdrawn (*21*). In contact coking, a moving bed of coke particles that grow to 10 mm. in diameter is used (*15*). The rounded particles produced by both processes have H:C ratios as low as 0.3.

Present conversions that decrease carbon number also affect H:C ratio. The reactions typical of catalytic cracking and coking fall diagonally in Figure 4. Some molecules crack to naphthas, but in doing this they rob hydrogen from others; these then undergo intermolecular dehydrogenation and increase in size as they become richer in carbon. Cycle oil or uncracked gas oil from catalytic cracking is too poor in hydrogen to be recycled, but too rich to be coked. Fortunately it makes a fair fuel.

Increasing Size. Two conversion processes, polymerization and alkylation, increase carbon number with little change in H:C ratio. Both start with olefins and are catalyzed by acids.

Polymerization, the earliest of the catalytic conversions, uses phosphoric acid in some form as catalyst. The polymer produced from gaseous olefins is nearly all gasoline. Even before World War II most refineries polymerized mixed propylene and butylene made in thermal cracking. During the war many refineries polymerized butylene only and several hydrogenated the butylene dimer to hydrocodimer for aviation gasoline. Since the war, polymerization of mixed olefins is again customary; catalytic cracking is now the major source, and the mixtures are richer in propylene. Nearly 200 polymerization units are in operation; technical advances in recent years have been few.

Alkylation of isobutane with olefins of three to five carbons uses sulfuric acid or hydrogen fluoride as the catalyst. The alkylate produced is nearly all gasoline of high octane number. About 30 alkylation units were built during the war to make isooctane for aviation

gasoline from the large amounts of isobutane formed in catalytic cracking. Afterward some units were shut down for several years. The increasing octane number of motor gasoline is bringing these back on stream and several new ones are being built. Among the few recent advances are improvements in mixing acid and hydrocarbons—not easy because the difference in specific gravity is about threefold—and the successful use of 85 per cent sulfuric acid instead of the conventional 95 per cent (*10*).

Ethylene is not usually converted to gasoline. Although two alkylation processes for doing so have been developed, little ethylene is available in concentrations above 10 per cent and enriching it is expensive. With isobutane, thermal alkylation of ethylene gives neohexane, and catalytic alkylation gives diisopropyl (*2*). The latter has an octane number well above 100 and recent advertising claims that it is now used in gasoline.

Conversions Affecting H:C Ratio

Octane numbers of gasolines have steadily increased until premium gasolines now rate above 92. Heavy naphthas distilled from petroleum often rate no more than 40 and contain *n*-alkanes that rate far below zero. Thermal reforming of heavy naphtha once sufficed to raise the octane number; by merely cracking out some of the *n*-alkanes, ratings as high as 70 could be reached. Half measures no longer suffice; hydrocarbons well above 100 octane number are needed in large quantities to satisfy present high-compression engines—let alone future ones with still higher compression ratios. Because most arenes in the gasoline boiling range have octane numbers above 100, they are the objective of today's fastest-growing conversion process—catalytic reforming. In much the same way that catalytic cracking improved upon thermal cracking, catalytic reforming is swiftly replacing thermal reforming.

Catalytic Reforming. Arenes are formed in catalytic reforming principally by three reactions. Easiest to carry out is the dehydrogenation of cyclohexanes; harder is the isomerization of cyclopentanes to cyclohexanes and dehydrogenation of these; most difficult is the cyclization of alkanes. Catalysts differ widely in ability to accomplish them.

These reactions that liberate hydrogen are not the only ones that occur. Cracking, favored by higher temperatures, and saturation of olefins are side reactions that consume hydrogen. When dehydrogenation proceeds too far, coke deposits upon the catalyst. Higher hydrogen pressures decrease coke formation but only at the expense of dehydrogenation. The several catalytic-reforming processes that have been devised have sought various balances among these many reactions.

Catalytic-reforming Processes

	Platinum catalyst			
Process	*°F.*	*P. s. i.*	*Regeneration*	*Reference*
Platforming	875	600	None	(*22*)
Catforming	900	500	Occasional	(*8*)
Ultraforming	950	300	Periodic	(*7*)

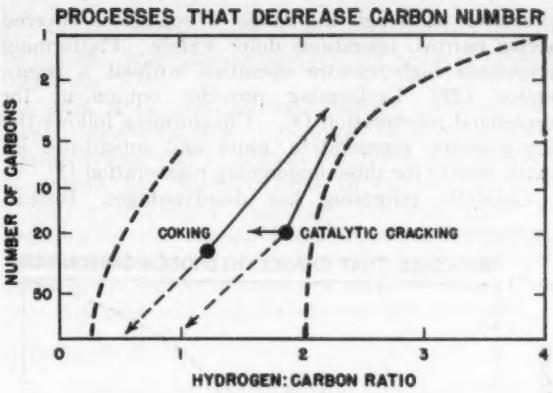

Figure 4

Molybdena supported upon alumina was the first reforming catalyst used. Eight units produced most of the toluene needed in World War II. Dehydrogenation of cyclohexanes predominated, and only at high temperatures and low pressures were high concentrations of arenes obtained. Cracking consumed much hydrogen, and so much coke formed that the catalyst had to be regenerated frequently.

Less than 1 per cent platinum supported upon alumina is a better catalyst. It converts cyclopentanes as well as cyclohexanes to arenes. Use of high hydrogen pressure almost prevents coke from forming at all. If the temperature is kept low, little cracking occurs and a good yield of hydrogen is obtained. With luck, a catalyst need not be regenerated for years.

Under suitable conditions platinum catalysts can cyclize alkanes as well as dehydrogenate cycloalkanes. Low pressure, high temperature, and active catalyst must be used. Because these conditions lead to coke formation, the catalyst must be periodically regenerated. Only by use of techniques that go beyond burning off the coke can the catalyst be kept sufficiently active. But gasolines of higher octane number can be obtained thus in greater yields than in any other way (*19*).

A serious engineering problem in catalytic reforming is how to supply the endothermic heat of dehydrogenation. Fixed-bed processes usually use two or more reactors with intervening furnaces to reheat the reactants. Use of a fluidized catalyst offers a way of obtaining isothermal reaction and a fluid-molybdena unit recently began operation (*17*); a fluid-platinum process seems inevitable, but as yet none has been announced.

Ten catalytic-reforming processes have been described. About 100 units are either in use or under construction in the United States; when all are on-stream, they will reform more than half the available heavy naphtha. Characteristics of three platinum-catalyst processes are given in the table, where the arrangement is by increasing temperature, or decreasing

pressure. Although the range of conditions covered seems narrow, operations differ widely. Platforming represents high-pressure operation without a regenerator (*22*). Catforming provides equipment for occasional regeneration (*8*). Ultraforming follows the low-pressure regenerative route and substitutes an extra reactor for those undergoing regeneration (*7*).

Catalytic reforming has disadvantages. Instead

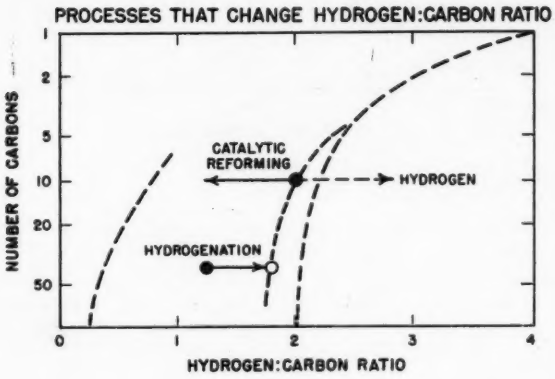

Figure 8

of making more gasoline, as catalytic cracking does, it destroys some hydrocarbons that already boil in the gasoline range. Heat content is greatly reduced by removal of hydrogen. The gains in engine power and performance provided by the higher octane number barely offset these sacrifices.

Hydrogenation. But the hydrogen made available by catalytic reforming is a decided asset. Some is already being converted to ammonia, but eventually most will be used in petroleum refining. Figure 5 shows why. Conversion of naphtha to arenes produces hydrogen that can convert a heavier extract to a stream as rich in hydrogen as petroleum. Because of the different carbon numbers, one mole of naphtha gives enough hydrogen to improve three to four moles of the heavier extract. On the other hand, entirely too little hydrogen is produced to convert much carbon to naphtha. Hydrogen from catalytic reforming is most likely to be first used in upgrading petroleum streams that already contain almost as much hydrogen as needed. Hydrogenations that reduce carbon number require so much more hydrogen that they will not appear in petroleum refineries as soon.

Conversions Affecting Neither Carbon Number nor H:C Ratio

The last class of conversions are those that change structure only. These processes are the isomerizations of alkanes, alkenes, and arenes.

The alkanes in petroleum are less branched than thermodynamic equilibrium requires. Isobutane was made from *n*-butane for use in alkylation during World War II but most of it now comes directly from natural gas. Because octane number of alkanes depends upon branching, treatment of pentane and hexane with active catalysts, such as aluminum chloride, increases the octane number. Should higher octane numbers require them, ways for isomerizing alkanes above seven carbons will probably be devised.

Alkenes produced from gas oil by thermal cracking were mostly straight chains with a double bond near the end. Isomerization of the double bond and chain increased octane number, but not much. Alkenes formed in catalytic cracking are near thermodynamic equilibrium; isomerizing them holds no promise.

The high octane numbers of all arenes leave little incentive to isomerize one to another for use in gasoline. Demand for individual arenes as chemicals does provide an incentive. For example, the meta isomer predominates in the xylenes made from petroleum, whereas the ortho and para isomers are most desired as chemical intermediates.

Introduction of catalytic conversions into petroleum refining emphasizes separations and simplifies finishing. Thermal conversions were not critical of the compositions of streams and the impurities in them. Catalytic conversions are affected by both; hydrogen-poor hydrocarbons form coke easily, and polar derivatives poison catalysts. At one time, such substances were removed, if necessary, as a final step and were discarded. The trend today is toward removing them before conversion and selling them if possible. Consequently, fewer impurities reach the finishing step.

FINISHING

Petroleum finishing has progressed far since "acid and caustic" was the only method used. Processes for bringing products up to specification quality have become more numerous. Color and odor; freezing point, vapor pressure, and boiling range; chemical composition and combustion behavior—these are but a few of the properties that must be checked and controlled constantly. The tasks of measurement and recording are tedious and automatic devices are being used wherever possible.

Two main problems must be overcome before products leave the refinery: (1) small amounts of impurities remaining must be removed, and (2) undesirable reactions that may occur in storage or service must be prevented. Treating methods remove the impurities; additives prevent the undesired reactions.

Treating

Compounds of sulfur, nitrogen, and oxygen are the major impurities in petroleum; the amounts differ widely with the source. On the average, there is about one such atom for every 100 carbon atoms. Many 25-carbon molecules, half the 50-carbon molecules, and almost all the larger molecules are not hydrocarbons at all. Metals also are found, even in distillates.

Sulfur is the most abundant impurity. During separation and conversion processes, hydrogen sulfide

from decomposition of sulfur compounds collects in the hydrocarbon gases. Several refineries are recovering sulfur from this source by controlled oxidation (*1*). New sweetening processes for eliminating mercaptans or thiols are replacing the lead oxide reagent used in the old doctor process. Air is the oxidizing agent, and copper chloride is the usual catalyst (*16*). Less reactive sulfur compounds, in which the sulfur is buried in rings, require more drastic methods. The best known of these is hydrofining with rugged metal-sulfide catalysts (*3*). Two molecules of hydrogen are consumed, one for the sulfur and the other to saturate the vacated linkages. The hydrogen may be supplied either from outside sources or by simultaneous partial dehydrogenation of the stream.

Nitrogen and metals are often associated as porphyrin complexes. In most crude petroleum the amounts of both are small but important. Ammonia and amines poison the acid catalysts used in polymerization and the metals poison cracking catalysts. They may remain undetected, and the consequences are easily attributed to blameless factors. Methods of removing them from crude oil, although needed, have not yet been widely adopted.

Oxygen compounds have been given little attention. However, phenols are often recovered from cracked naphthas by scrubbing with caustic.

In service, some nonhydrocarbons are desirable in petroleum products and not all hydrocarbons are desirable. Nitrogen and oxygen compounds inhibit oxidation of stored fuels, but the effect is small and better protection is afforded by adding synthetic inhibitors. Highly unsaturated hydrocarbons that may oxidize to acids or polymerize to gums are now frequently removed with spent conversion catalysts: sulfuric acid from alkylation instead of fresh acid, and silica-alumina from catalytic cracking instead of clay.

Particularly undesirable in petroleum products are polycyclic arenes that cause tumors in laboratory animals. Although rare in crude petroleum, small amounts of carcinogens occur in the high-boiling hydrogen-poor products from some catalytic conversions. They contain 20 or more carbons, boil between the fuels and lubricants, and are removed in the refining of both. Streams from catalytic cracking that might contain them are recycled through the units where they are adsorbed upon the catalyst and are burned during regeneration. Other streams suspected of containing them are coked or burned in the refinery as fuel.

Additives

Inhibitors, soaps, polymers, and other additives have improved stability, detergency, viscosity, and other properties of lubricants for years. The practice now extends to other products. Use of rust preventives in diesel fuels is an example. Some additives control deterioration before use and others affect behavior during use.

Oxidation is the most important reaction against which products need protection. Only recently has the speed with which most hydrocarbons oxidize in air become appreciated. The knowledge has yet to be applied, but it has emphasized the value of present inhibitors.

Control of the combustion of fuels by traces of semi-combustible substances is a busy field of research. Tetraethyllead has been used for years and tricresyl phosphate has recently been promoted. All such additives are mixed blessings. Research aimed at determining the circumstances in which advantages outweigh disadvantages is fantastically complicated. Refiners are rightly reluctant to adopt new ones until thorough studies in each of their own fuels are made.

CONCLUSION

In retrospect, petroleum refining has changed markedly since World War II. Replacement of thermal by catalytic conversions, barely started then, is perhaps two-thirds complete. Diesel fuels instead of coal run the railroads. Manufacture of chemicals has become integrated with refining. New knowledge of separations and conversions is ready for application where needed. Looking ahead, one asks how the next decade can possibly advance as far—until one remembers that that was the very question asked a decade ago.

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A GENERAL EQUATION FOR APPROXIMATE HYDRONIUM ION CALCULATIONS

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THE calculation of hydrogen ion concentration in a solution containing a weak electrolyte is a difficult one for the average student first facing this problem. The main source of trouble is the variety of equations he is given to use for different cases involving weak acids or bases, alone or with their salts. Part of the difficulty can be avoided by the Brönsted approach; thus see the equation of DeFord:[1]

$$[H_3O^+] = K_a \frac{C_a - [H_3O^+] + [OH^-]}{C_b + [H_3O^+] - [OH^-]} \qquad (1)$$

Here C_a and C_b represent the stoichiometric concentrations of any monoprotic Brönsted acid and its conjugate base, K_a the protolysis constant of the acid, and $[H_3O^+]$ and $[OH^-]$ the equilibrium concentrations of these ions. Equation (1) is very satisfactory when some terms may be neglected and when the student knows which terms these are. However, in many problems the student does not feel justified in neglecting any terms. He is then faced with the often painful trial-and-error solution of equation (1) or with the use of an approximation of uncertain validity.

The use of an approximate equation is really justifiable only if the student can be induced to treat his answer as a first approximation and to put it back into an exact equation (like equation 1) to get a second approximation. Whether or not this aim can be achieved, the use of *one* general approximate equation rather than of several of more limited range seems desirable. The following empirical equation is helpful:

$$[H_3O^+] = K_a \frac{C_a - \frac{1}{2}\sqrt{C_aK_a} + \sqrt{C_bK_b}}{C_b - \frac{1}{2}\sqrt{C_bK_b} + \sqrt{C_aK_a}} \qquad (2)$$

[1] DEFORD, D., J. CHEM. EDUC., **27**, 554 (1950).

This equation will not always give reasonable results, but it will do so under most conditions of practical interest. To test its applicability in a given case, find the larger of C_aK_a and C_bK_b; let us denote this by CK. Then (*a*), CK must exceed K_w, the ionization constant for water, or the pH will be controlled by the water (and will be near 7 at 25°C.); and (*b*), C must exceed K. Thus if C_aK_a is larger than C_bK_b, reasonable results will be obtained from equation (2) when C_aK_a exceeds K_w and when C_a exceeds K_a; in this case there are no restrictions on the relative values of C_b and K_b.

Equation (2) has been found to give better results than the various simple approximations often used for the calculation of the H_3O^+ concentration in solutions of a weak acid, a weak acid and its salt, a weak base, or a weak base and its salt. It is simple enough so that the average student much prefers using it to learning several equations for these "different types of solution"; and the use of one equation for all four types helps him to realize that these problems are not wholly unconnected but are merely one problem in various guises.

Equation (2) can also be recommended for those planning to use the DeFord equation. Since in any problem involving successive approximations a good first approximation will greatly reduce the subsequent labor involved, the following procedure is recommended: use equation (2) to find the first approximation and thereafter use equation (1) until the H_3O^+ concentration has been found to the desired accuracy. As noted above, since equation (2) is only approximate, every effort should be made to persuade the student to do this in all cases.

RICHARD CHENEVIX (1774-1839) AND THE DISCOVERY OF PALLADIUM[1]

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RICHARD CHENEVIX was born in Ballycommon, King's County (now Leix), Ireland, not far from Dublin, in 1774. He was of Huguenot extraction, and his family were French refugees from the Edict of Nantes. He attended the University of Glasgow in Scotland, and later spent much of his life in France.[2]

Evidence of his early years in France is provided in Chenevix's own book, "Remarks Upon Chemical Nomenclature According to the Principles of the French Neologists," published in London in 1802. On page 148 he says, "When I was in Paris, where there is so much opportunity for acquiring true scientific chemical instruction, I had opportunities of making observations in three schools, where chemistry was taught."

He then proceeds to comment on the lectures given by professors in the three schools. The same book gives further evidence of his French education by indicating his good knowledge of the French language. He says, for instance, on page 188:

> The E mute is one of the characteristic features in the peculiar pronunciation of the French; and which, in the mouth of a native, contributes much to the variety and perspicuity of the language. It is even one of the fundamental sources of harmony in French versification.

Thomas Thomson[3] related that Chenevix happened to be in Paris during the Reign of Terror, and was thrown into prison and put into the same cell with several French chemists whose main topic of conversation was chemical in nature. "He caught the infection," as Thomson put it, and after his release from prison began to study the subject with much energy and success, and before long became noted especially as an analytical chemist.

ANALYTICAL WORK

His first paper in English,[4] published in 1801, was an analysis of a new variety of lead ore, the muria-carbonate. Shortly afterward he was responsible for a series of analyses of the arsenates of copper.[5] Though his techniques for separating and estimating the quantity of acidic radicals present are crude by modern standards, he demonstrated that several different species of copper arsenates existed.

Crystalline alumina occurs in nature as the mineral corundum. There are three main varieties, distinguished by structure and degree of purity. First are the transparent or translucent gem-stones named according to their colors, the ruby (red or reddish, because of the presence of chromic oxide) and the sapphire (blue, yellow, or green). Second is common corundum, which is transparent and of variable tint, and third is emery, a kind of granular corundum mixed with magnetite or hematite. In 1777 T. Bergman analyzed sapphire and reported specific percentages of alumina, silica, calcium oxide, and iron oxide. In 1802 Chenevix reported on detailed analyses of sapphire, ruby, and corundum, and stated that 5 to 7 per cent silica was also present.[6] His figures are not significantly out of line with modern work, though some of his high silica content was apparently derived from the agate mortar used in the grinding of his samples.

PALLADIUM ANNOUNCEMENT

In 1803 there was circulated through the English-speaking scientific world a notice of a very strange type. This anonymous handbill told of the isolation of a new chemical element, and was phrased in these terms:

> Palladium, or new silver, has these properties among others that show it to be a noble metal.
>
> (1) It dissolves in pure sprit of nitre, and makes a dark red solution.
> (2) Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua regia.
> (3) If you evaporate the solution you get a red calx that dissolves in spirits of salt or other acids.
> (4) It is thrown down by quicksilver, and by all metals but gold, platinum, and silver.
> (5) Its specific gravity by hammering is only 11.3; but by flatting, as much as 11.8.
> (6) In a common fire, the face of it tarnishes a little, and burns blue, but becomes bright again, like the other noble metals, on being stronger heated.
> (7) The greatest heat of a blacksmith's fire would hardly melt it.
> (8) But if you touch it, while hot, with a small bit of sulfur it runs as easily as zinc.
>
> It is sold by Mrs. Forster, at No. 26, Gerrard Street, Soho, London; in samples of five shillings, half a guinea, and one guinea each.[7]

[1] Presented before the Division of the History of Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[2] KOPP, *Geschichte der Chemie*, 4, 227–8; REILLY, D., "Three Centuries of Irish Chemists," Cork, Ireland, 1941, p. 12; WEEKS, M. E., "Discovery of the Elements," 5th ed., Journal of Chemical Education, Easton, Pa., 1945, pp. 217–18.

[3] THOMSON, THOMAS, "History of Chemistry," London, 1831, Vol. 2, pp. 215–17.

[4] *Nicholson's J.*, 4, 219–23 (1801).

[5] *Phil. Trans.*, 1801, 169–92, 193–240; *Ann. Chim.*, 45, 44–61 (1802).

[6] *Phil. Trans.*, 1802, 327–47; *J. de phys.*, 55, 409–26 (1802).

[7] *Phil. Trans.* 1803, 290–320.

Some additional information on the new material was given in an editorial comment in *Nicholson's Journal:*[8] "Mrs. Foster [Forster?] it appears," wrote the editor, "is only the vendor, and totally unacquainted with the person who brought the metallic substance and the printed paper to her house—I received a small piece by the post. The price of the specimen was at the rate of above one shilling per grain."

Richard Chenevix by this date had some 16 scientific publications to his credit in both British and French journals, and was well known as a leading analytical chemist. In addition, his first book (mentioned earlier), "Remarks upon Chemical Nomenclature According to the Principles of the French Neologists," had won him notice as a pioneer writer on chemical nomenclature. He had just been elected a Fellow of the Royal Society and of the Royal Irish Academy.

Chenevix felt sure that some fraud was involved in the palladium announcement in view of the curious way in which its discovery was announced. He went to Mrs. Forster's and purchased her complete stock of the new material, 332 grains, for 15 guineas. He set out to examine it, prepossessed with the idea that it was an alloy of some two known metals.

He checked the properties claimed for the material and found them to be as stated. He wrote to Vauquelin, professor of chemistry in Paris, told him of his plans for further work on the material,[9] and enclosed some small samples of the chemical. Vauquelin checked the properties also, and cautiously stated that he believed palladium in fact might be a new element. He would, however, withhold his opinion till Chenevix had carried out more extensive tests on the material.

CHENEVIX DRAWS CONCLUSIONS

After a laborious series of experiments, Chenevix concluded that palladium was in fact a compound of either platinum or mercury or an amalgam of platinum made in a peculiar way. He communicated his results to the Royal Society, where they were read as a paper by Dr. William Hyde Wollaston (1766–1828), who was secretary at the time.

In Chenevix's paper he spoke of the original palladium announcement as "an imposition...not, as was shamefully announced, a new simple metal," and nothing more than "a contemptible fraud." He claimed in fact that by altering the proportions of mercury and platinum in alloys he prepared, he had synthesized the alleged palladium.

Chenevix's report caused a scientific sensation and was widely reprinted.[10] His conclusions were at first readily accepted, and the synthesis of palladium became a popular pursuit in continental laboratories. However, all was not clear sailing for long, as a note of doubt crept into some chemists' minds, especially in view of the fact that Vauquelin was unable to find any positive results in testing for either platinum or mercury on the small pieces of palladium at his disposal.

Soon afterwards Klaproth wrote, refusing to agree with Chenevix's synthesis. Vauquelin and Fourcroy, unable to find mercury in palladium, suggested that perhaps it might be an alloy of platinum and some new element. Joseph Hume wondered if tungsten might not be involved.[11]

When the discussion was in progress, a new anonymous notice appeared in London.[12] This offered a reward of twenty pounds to anyone who could make twenty grains of palladium by Chenevix's process, or by any other process whatsoever.

No one came forward to claim the reward, and soon afterward Dr. Wollaston read a paper to the Royal Society describing his isolation of a new metal, rhodium, from crude platinum ores.[13] He also mentioned that he had been able to separate a small amount of palladium from the same ore.

Wollaston stated that the presence of traces of palladium in crude platinum ores might have led Chenevix astray in his much publicized amalgam experiments. As far as he, Wollaston, was concerned, he had found it impossible to prepare palladium by the Chenevix method.

In his rebuttal[14] Chenevix still insisted that palladium was an alloy, though he did admit that it had required about 1000 experimental trials in order to secure four actual syntheses by his method. Actually, it has been stated elsewhere[15] that Chenevix spent about 14 hours a day in the laboratory while following through this work.

The next step in the drama was a signed letter by Wollaston in *Nicholson's Journal*[16] admitting that he had been the author of the original anonymous notice of the discovery of palladium and also of the later notice offering a reward for the synthesis of palladium. The details of the work, as outlined by Wollaston, made it quite clear that palladium was in fact a new element.

Chenevix's error was due in great part to his preconceived idea that the discovery of palladium was a hoax. It may also have been a result, as Wollaston suggested, of the fact that Chenevix actually isolated some palladium from crude platinum without realizing its presence there, and was thus misled into the belief that he had produced it artificially.

It seems to a modern observer that Wollaston was at least doing something questionable in allowing Chenevix to present his original "amalgam" paper at the Royal Society while he himself was secretary of that body. Thomson says that Wollaston made every effort to dissuade Chenevix from presenting his paper, short, however, of telling him the full facts of his own discovery.

Why did Wollaston find it so necessary to hide the

[8] ANON., *Nicholson's J.*, **5**, 136 (1803).
[9] CHENEVIX, R., *Ann. chim. et phys.*, **46**, (1) 333 (1803).
[10] *Ann.*, **47**, 151–202 (1803); *J. des Mines*, **14**, 372–408 (1803); *J. de Phys.*, **57**, 127–39, 217–28 (1803).
[11] WHITE, A. M., AND H. B. FRIEDMAN, J. CHEM. EDUC., **9**, 236–45 (1932).
[12] ANON., *Nicholson's J.*, **6**, 117 (1804).
[13] WOLLASTON, W. H., *Phil. Trans.*, **94**, 419 (1804).
[14] CHENEVIX, R., *Phil. Trans.*, **95**, 104 (1805).
[15] THOMSON, THOMAS, *Phil. Soc. Glasgow*, **3**, 139 (1850).
[16] WOLLASTON, W. H., *Nicholson's J.*, **10**, 204 (1805).

facts? Wollaston was not a rich man, and had conceived the idea of preparing pure fabricated platinum so that it could be used for laboratory ware. He made a moderately large investment in crude platinum, and finally succeeded in making malleable platinum. He kept the process a secret and exploited it for his financial advantage. In his work he discovered two new elements, palladium and rhodium. Were he to announce the discovery of these elements routinely, his secret might be lost, as others would then find means of purifying crude platinum. He chose the anonymous method of announcing the existence of palladium to gain priority without losing his advantage in the platinum purification field.

Wollaston, his reputation enhanced by his two discoveries, went on to win further prominence in chemistry. Richard Chenevix, his reputation badly damaged, left England and lived in France for the remainder of his life. He published fewer papers in those later years, although his papers on "Observations on the mineralogical systems," in which he attacked Werner and upheld Haüy, were significant.[17] In addition, in 1809 he won some distinction in the history of organic chemistry by preparing acetone by distillation of acetate.[18]

In later years he turned to literary work, and published a comedy, "Mantuan Revels," a historical tragedy, "Henry VII," and "Leonora and other Poems," as well as "An Essay Upon Natural Character," which appeared after his death in Paris on April 5, 1830.[19]

[17] *Ann. chim.* (*Paris*), **65**, 5–43, 113–160, 225–277 (1808).

[18] *Ann. chim.* (*Paris*), **69**, 5–58 (1809); GILBERT, *Ann.*, **32**, 156–201 (1809).

[19] *Roy. Soc. Catalogue of Sci. Papers*, 1800–63, 1867, I, 895–6, lists 26 papers by Richard Chenevix.

PREPARATION OF ANHYDROUS PYRIDINE HYDROCHLORIDE

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RECENTLY the use of pure anhydrous pyridine hydrochloride was required in this laboratory. The usual procedure for preparing such compounds, *i. e.*, neutralizing an aqueous solution of pyridine with hydrochloric acid and evaporating the water, is time-consuming and fails to yield an anhydrous product. Pyridine hydrochloride is very hygroscopic. The procedure described below is much more convenient and gives a high yield of essentially pure material. It should prove suitable as an exercise in inorganic preparations for advanced students.

A 20–40 per cent solution of pure pyridine in anhydrous ether is treated with gaseous hydrogen chloride until precipitation is complete.

$$C_5H_5N + HCl \rightarrow C_5H_5N \cdot HCl$$

Pyridine hydrochloride is quantitatively insoluble in ether. The excess ether is distilled away on a steam bath and finally quantitatively removed by pumping the salt *in vacuo* in a vacuum desiccator. The crystals, when first prepared, have the appearance of pure dry sodium chloride. They absorb moisture readily and become sticky, however, if not rigorously protected from the atmosphere.

In a typical preparation 69.0 g. of anhydrous pyridine was dissolved in 200 ml. of anhydrous ether in an 800-ml. beaker. Seventy-five ml. of concentrated hydrochloric acid and 50 g. of NaCl were placed in a dry 500-ml. wide-mouth Erlenmeyer flask. The Erlenmeyer flask was closed with a rubber stopper through which was inserted the stem of a 100-ml. dropping funnel, a piece of glass tubing bent in a right angle to serve as a delivery tube, and a straight piece of glass tubing. Twenty-four ml. of concentrated sulfuric was poured into the dropping funnel, which was closed by a one-hole rubber stopper carrying a glass tube. Rubber tubing connected the top of the dropping funnel and the top of the Erlenmeyer flask and served as a pressure equalizer. The outlet tube from the Erlenmeyer flask was connected with rubber tubing to a four-inch funnel which dipped into the ether solution of pyridine.

The sulfuric acid was run slowly into the hydrochloric acid solution so that the HCl would not be generated faster than it could be absorbed. The ether solution of pyridine was cooled to prevent the large heat of reaction from boiling the mixture. There resulted 98.5 g. of 99.8 per cent pure (m.p. = 143.4) pyridine hydrocholoride, which amounted to a 98.5 per cent yield. Heilbron[1] lists the melting points as 82°C. The material was analyzed for chloride by precipitating silver chloride and for pyridine by the technique suggested in *Chemical Abstracts*.[2]

Pyridine hydrochloride is soluble in pyridine and its solubility increases rapidly with temperature. A saturated solution contains 0.113 g./ml. at 30° and 0.1758 g./ml. at 50°C.

[1] HEILBRON, I. M., "Dictionary of Organic Compounds," Oxford University Press, New York, 1938, Vol. III.

[2] *Chem. Abstracts*, **19**, 2181 (1924).

A SEQUENCE OF SYNTHESIS IN THE GENERAL ORGANIC LABORATORY CLASS

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BEGINNING organic chemistry students can receive valuable synthetic experience by completing a sequence of preparations in which a compound that has been prepared is used as starting material for the next operation. Experience indicates that students do well and are interested in such procedures if the chosen compounds are of practical importance and if the procedures can be accomplished without undue difficulties.

The following sequence of reactions has been successfully performed by beginning students. The series illustrates a number of procedures common to aromatic chemistry: oxidation, esterification, nitration, reduction, and cyclization. The starting material was *p*-xylene (95 per cent, from Oronite Chemical Company) which was oxidized to terephthalic acid. This oxidation is practically quantitative and is not much more difficult to accomplish than the usual preparation of benzoic acid. It was found that the oxidation proceeds slowly over a water bath, but by using an oil bath at 120° to 130°C. the oxidation can be completed in five to six hours.

Part of the terephthalic acid was treated with PCl_5. The chlorination product in turn was slowly added to methanol, which was then diluted with water, yielding crystals of dimethylterephthalate. This compound is today of tremendous commercial importance in the manufacture of synthetic fibers.

The remaining terephthalic was nitrated with concentrated HNO_3 and fuming H_2SO_4. If the usual preparation of nitrobenzene has already been done by the students, this procedure is of value in noting the differences in nitration conditions owing to the deactivating effects of the two carboxyl groups. This step results in the lowest yield but most students reported 60 per cent or better.

The nitroterephthalic acid is easily reduced to aminoterephthalic acid by refluxing with HCl and stannous chloride. The aminoterephthalic acid is a convenient starting material for the preparation (via cyclization) of 4-quinazolone-7-carboxylic acid which offers the possibility of other interesting syntheses.

PROCEDURES

(1) *Oxidation of p-Xylene.* In a two-liter flask equipped with a stirrer and reflux condenser were placed 15 g. of *p*-xylene, 10 g. NaOH, 90 g. $KMnO_4$, and one l. of water. This mixture was refluxed at 120°C. until the color of $KMnO_4$ was no longer visible. The oxidation mixture was filtered to remove the MnO_2, washed, and the filtrate acidified with dilute H_2SO_4. The crude terephthalic acid was filtered, washed, dried, and used for the next preparation; yield, 20 g. (85 per cent).

(2) *Nitration of Terephthalic Acid.* Ten g. of crude terephthalic acid, 50 ml. of fuming H_2SO_4, and 50 ml. of conc. HNO_3 were placed in a 250-ml. beaker. The mixture was heated until all of the acid went into solution and then allowed to cool. The cooled mixture was poured over cracked ice. The precipitate of nitroterephthalic was collected on a filter, washed with water, and dried. A sample recrystallized from water melts at 269–70°C. Yield, 9.3 g. (73 per cent).

(3) *Esterification of Terephthalic Acid.* One g. of terephthalic acid was carefully heated in a test tube with one g. of PCl_5 until the mixture was melted. The mixture was carefully poured into 15 ml. of methanol.

The methanol was diluted with water until the precipitate of dimethylterephthalate appeared. The ester was filtered, washed with water, and dried. Recrystallization from methanol produced beautiful white needle-like crystals melting at 140°C.

(4) *Reduction of Nitroterephthalic Acid.* To a hot solution of 30 g. of $SnCl_2$ in 100 ml. of conc. HCl was added 8 g. of nitroterephthalic, and the mixture was refluxed over a water bath for one hour. Upon cooling the aminoterephthalic was precipitated. The acid was filtered, washed with cold water, and dried. The aminoterephthalic acid is a lemon-yellow solid which melts with decomposition above 300°C. Yield, 5.9 g. (89 per cent).

(5) *Preparation of 4-Quinazolone-7-Carboxylic Acid.* When 5 g. of aminoterephthalic acid is heated with a slight excess of formamide, a gelatinous mass is obtained from which the quinazolone carboxylic acid is obtained by recrystallization from water. It melts with decomposition above 300°C.

UNIVERSITY INORGANIC CHEMISTS

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THE names and major research interests of the chemistry faculties of 90 institutions which offer doctoral degrees in chemistry are included in a recent, very useful publication[1] by the A. C. S. Committee on Professional Training. It is stated that the 90 are a majority of all such institutions. The following facts about research inorganic chemists have been obtained from the data of this report.

Chemistry staff members listing their sole specialization as inorganic chemistry number 143. Those listing inorganic chemistry together with some other specialization, usually physical chemistry, number 45, making a total of 188 who, by their own judgment, might be classified at least partly as inorganic chemists. These are the individuals about whom the following summary has been prepared.

These chemists have received their Ph.D. degrees at a total of 46 institutions, but more than half of the degrees were from only seven. The University of Illinois leads with 27, followed by the University of Chicago, 16, University of California, 16, Cornell University, 11, University of Wisconsin, 10, Massachusetts Institute of Technology, 10, and Ohio State University, eight. In other words, one in seven of today's university research inorganic chemists received his doctoral training at Illinois; one in 23 at Ohio State. One in five is now teaching in the same institution at which he earned the degree of doctor of philosophy.

More than half (96) of the university inorganic chemists are more than 40 years of age; one-third (62) are 35 or less.

Of the 188 inorganic chemists, 40 appear to have published no research results during the last five years. This leaves 148 to be considered active in research.

Specific research interests, naturally, vary widely. However, certain general topics appear to be especially popular, as indicated by the number of men listing them. Coordination complexes are of research interest to 34 per cent of those active in research, nonaqueous solvents to 20 per cent, hydrides to 15 per cent, rare earths to nine per cent, ion exchange to six per cent, "less familiar elements" to six per cent, and molecular addition compounds to five per cent.

Within the first nine months of 1953 (the only period definitely determined by the available data), research papers by 73 inorganic chemists at universities appeared. Only five of these chemists had more than four publications within this period, and most (53) had but one or two.

Of the 90 institutions, only 74 offer advanced degrees in inorganic chemistry. Some of the universities which do have inorganic chemists do not provide such training. On the other hand, it is noteworthy that eight of the 74 actually list not a single staff member having inorganic chemistry as a major interest.

Opinions will vary as to what extent the above facts are good, bad, or indifferent, but they seem worth thought.

[1] "Faculties, Publications, and Doctoral Theses in Chemistry and Chemical Engineering at United States Universities," prepared by the Committee on Professional Training, American Chemical Society, 1953.

THE ORIENTATION AND MECHANISM OF ELECTROPHILIC AROMATIC SUBSTITUTION[1]

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For over fourscore years now, chemists have been fascinated by the fact that substitution reactions with monosubstituted benzenes yield varying amounts of ortho, meta, and para isomeric disubstitution products, depending primarily upon the nature of the group already attached to the benzene nucleus. It was early recognized that groups could be classified as chiefly ortho- and para-directing or meta-orienting, and much effort was spent in arranging substituents in order of their orienting effects. This is a topic which every student of organic chemistry takes up briefly, learning at least one of the many empirical rules[2] by which one may predict the orienting influences of the various types of substituents.

What has increased the attractiveness of this topic is the recognition that most of the chemical and physical properties of aromatic molecules also are dependent upon the nature of the nuclear substituents. In this connection, there have been observed good correlations between orientation of aromatic substitution and such properties as dipole moments,[3] wave length[4] and intensity[5] of ultraviolet light absorption, infrared absorption frequencies,[6] nuclear magnetic shielding,[7] dissociation constants of phenylacetic acids, benzoic acids, phenols, anilines, phenylboric acids, etc.,[8] oxidation potentials of quinones,[9] and many chemical reactivities as expressed through the Hammett equation.[10] This suggests that essentially the same basic factors are responsible for each of these properties; consequently, the broad problem has been to identify these factors and to study their operation.

Many reviews have appeared on aromatic substitution[2, 11, 12, 13] but the subject is one of such continued popularity that it seems worth while to present to the student some of the most recent concepts and experimental results in this area.

Although substitution may take place by either electrophilic (electron-seeking) or nucleophilic reagents, or by free radicals (homolytic) attacking the aromatic molecule, the type first mentioned is by far the most common and extensively studied, so that this article will be limited to electrophilic substitution. Furthermore, the discussion will be directed to the two fundamental questions of interest to a chemist: (1) what is the mechanism of reaction and (2) why do groups show preferential orientation in substitution?

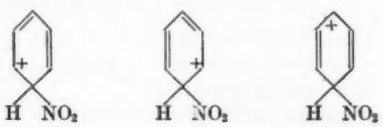
Nitration with the usual nitric-sulfuric acid mixture has been shown quite conclusively to proceed by the following mechanism:[11]

$$2H_2SO_4 + HONO_2 \rightleftharpoons 2HSO_4^- + H_3O^+ + {}^+NO_2 \quad (1)$$

$$ArH + {}^+NO_2 \xrightarrow{\text{slow}} {}^+ArHNO_2 \quad (2)$$

$${}^+ArHNO_2 \longrightarrow ArNO_2 + H^+ \quad (3)$$

where ArH is an aromatic compound and $^+ArHNO_2$ is a pentadienate cation[14] whose structure is a resonance hybrid of forms such as



Several types of experimental data provide evidence that the nitronium ion is the nitrogen species that attacks the aromatic molecule.[15] For instance, sulfuric

[1] Based on talks given, spring, 1954, before the Lund Chemical Society, University of Lund, Lund, Sweden, and the Danish Chemical Society, University of Copenhagen, Copenhagen, Denmark.

[2] Ferguson, L. N., *Chem. Revs.*, **50**, 47 (1952).

[3] Ri, T., and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940); L. E. Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[4] Doub, L., and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

[5] Platt, J. R., *J. Chem. Phys.*, **19**, 263 (1951).

[6] Soloway, A. H., and S. L. Friess, *J. Am. Chem. Soc.*, **73**, 5000 (1951).

[7] Meyer, L. H., and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

[8] Branch, G. E. K., and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, **1941**, p. 240 ff.; R. L. Heppolette and J. Miller, *J. Am. Chem. Soc.*, **75**, 4265 (1953).

[9] Fieser, L. F., and M. Fieser, *ibid.*, **57**, 491 (1935); **51**, 3101 (1929).

[10] Hammett, L. P., "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, **1940**, p. 186.

[11] Ingold, C. K., "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., **1953**, Chap. VI.

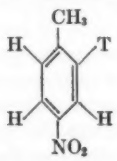
[12] Price, C. C., *Chem. Revs.*, **29**, 37 (1941).

[13] For earlier reviews, see references cited in Ref. 2. For reviews on nucleophilic substitution, see J. Miller, *Revs. Pure and Appl. Chem.* (*Australia*), **1**, 171 (1951); J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951). For a recent treatment of homolytic substitution, see D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1952).

[14] This name for the intermediate complex of electrophilic substitution is taken from M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, **1949**, p. 164.

[15] Frost, A. A., and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, **1953**, p. 297 ff.

acid solutions of nitric acid give a van't Hoff *i* factor of four, supporting equation (1), and in addition, the partial pressure of nitric acid in excess sulfuric acid diminishes to zero, showing that nonvolatile products are formed. Moreover, sulfuric acid solutions of nitric acid have a very high conductivity with nitric acid migrating to the cathode. Finally, Raman spectra establish the presence of nitronium ions as the chief nitrogen moiety in sulfuric acid solutions. This was supported by the isolation and Raman spectra of nitronium perchlorate and nitronium bisulfate. The strongest evidence that step (2) is the rate-determining step comes from kinetic data, where it is found that the rate-determining step must not involve a change in the number of cations and that the rate of nitration of all compounds parallels the concentration of nitronium ions. There is strong evidence[16] to show that (3) is not the slow step in nitration, from the fact that in the nitration of 2-tritium-4-nitrotoluene, protons and



tritium ions are eliminated at the same rate. Reaction occurs, of course, ortho to the methyl group, and if (3) were the slow step, then there should be a small but distinct difference in the rate of elimination of protons and tritium ions owing to a small difference in C—H and C—T bond energies.

In other solvents nitration apparently takes place by the same mechanism but the rate of production and the concentration of nitronium ions is much lower, sometimes the rate of production of nitronium ions becoming the slowest step. However, there is considerable data to support the above mechanism of nitration and it is satisfying that practically all data are consistent with this idea.

The mechanism of aromatic halogenation is far less clearly understood. The kinetics are fairly complex, being complicated by the facts that (1) the order of reaction with respect to halogen varies from one to four, depending upon the halogen concentration; (2) frequently heterogeneous catalysis is used (aluminum, iron, or their trihalide salts) and the liberated hydrogen halide also is a catalyst; and (3) different halogen species attack the aromatic molecule, depending upon the experimental conditions. In the last decade, considerable attention has been given to aromatic halogenation,[17] from which it appears that one of two mechanisms seems likely under most conditions, although others may occur. In acetic acid, water, and most solvents, it is probable that the neutral halogen molecule attacks the aromatic substance and reaction takes place by the three-step process:

$$\mathrm{ArH} + \mathrm{X_2} \rightleftharpoons \mathrm{ArH{:}X_2} \qquad (1)$$

$$\mathrm{ArH{:}X_2} + C \xrightarrow{\text{slow}} {}^{+}\mathrm{ArHX} + C\mathrm{X}^{-} \qquad (2)$$

$${}^{+}\mathrm{ArHX} \longrightarrow \mathrm{ArX} + \mathrm{H}^{+} \qquad (3)$$

where X is a halogen atom, *C* is a catalyst (AlX_3, HX, etc.), $ArH{:}X_2$ is a molecular addition complex (frequently called a pi complex), studied extensively in recent years by many authors,[18] and $^{+}ArHX$ is a pentadienate cation. In hypohalous acid it seems that a halogen cation or hydrated halogen cation is the halogenating species, and reaction takes place through a two-step process similar to that of nitration by nitronium ions. In any event, the arguments on the mechanism are too complex to be discussed here.

It has generally been regarded that alkylation and acylation take place by a three-step process in which a carbonium ion is first generated by the reaction of the alkyl or acyl halide with the catalyst,[12]

$$\mathrm{RX} + \mathrm{MX_3} \rightleftharpoons \mathrm{R}^{+} + \mathrm{MX_4}^{-}$$

$$\mathrm{ArH} + \mathrm{R}^{+} \xrightarrow{\text{slow}} {}^{+}\mathrm{ArHR}$$

$${}^{+}\mathrm{ArHR} \longrightarrow \mathrm{ArR} + \mathrm{H}^{+}$$

where R^+ represents an alkyl or acyl carbonium ion, $^{+}ArHR$ is a pentadienate cation, and MX_3 is a Friedel-Crafts type metal halide catalyst. Recently evidence has been presented[19] to raise doubt about the ionization of the organic halide and to suggest that the organic halide and catalyst form a 1:1 addition compound which reacts with the aromatic molecule; then the halogen of the organic halide is lost to the catalyst simultaneously with the formation of the aryl-alkyl carbon-carbon bond.

$$\mathrm{ArH} + \mathrm{RX{:}MX_3} \rightarrow \mathrm{HAr\cdots RX{:}MX_3} \rightarrow \mathrm{ArR} + \mathrm{HX} + \mathrm{MX_3}$$

Therefore, the mechanisms of alkylation and acylation are still not completely clarified.

Of course, other electrophilic reactions, such as sulfonation, mercuration, chloromethylation, etc., have been studied, but the prominent features of the mechanism of electrophilic aromatic substitution should be evident without discussing additional examples. Therefore, let us consider the second phase of this topic, namely, the orienting influences of substituents. Experimental conditions such as temperature, concentration of reactants, or type of solvent have only minor effects upon orientation and it appears that there are the following four important factors to be considered:

(1) Electron distribution of the normal aromatic molecule.

[16] MELANDER, L., *Nature*, **163**, 599 (1949).

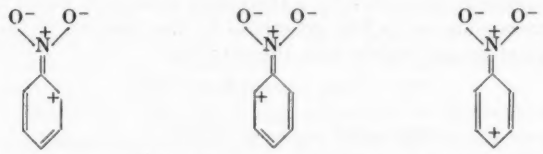
[17] ROBERTSON, P. W., ET AL., *J. Chem. Soc.*, **1954**, 1267, and previous papers; L. N. FERGUSON, A. Y. GARNER, AND J. L. MACK, *J. Am. Chem. Soc.*, **76**, 1250 (1954); R. M. KEEFER, J. H. BLAKE III, AND L. J. ANDREWS, *ibid.*, **76**, 3062 (1954); T. TSURUTA, K. SASAKI, AND J. FURUKAWA, *ibid.*, **74**, 5995 (1952); P. B. DE LA MARE, A. D. KETLEY, AND C. A. VERNON, *Research* (*London*), **6**, 12*S* (1953).

[18] FERGUSON, L. N., J. CHEM. EDUC., **31**, 626 (1954); L. J. ANDREWS, *Chem. Revs.*, **54**, 713 (1954).

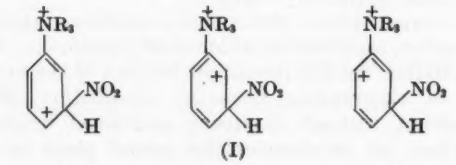
[19] BROWN, H. C., AND M. GRAYSON, *J. Am. Chem. Soc.*, **75**, 6285 (1953).

(2) Relative stabilities of transition states when reaction occurs at ortho, meta, or para positions.
(3) Steric effects.
(4) Nature of the reagent.

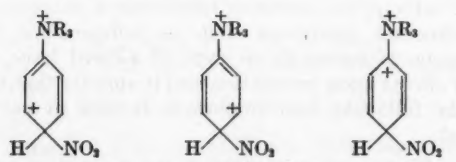
First of all, it is obvious that the reagents in these reactions under discussion are electrophilic because groups that increase the electron density of the benzene nucleus increase the rate of reaction, and groups that decrease the nuclear electron density diminish the rate of reaction. Therefore, other things being equal, the reagent will tend to react with the carbon atom at which there is the greatest availability of electrons. Now, a substituent alters the electron density of the ring through effects such as resonance and induction. For illustration, consider nitrobenzene. The strong electron-attracting nitro group withdraws electrons from the ring to decrease the over-all nuclear electron density and makes nitrobenzene less reactive than benzene. Then, owing to resonance among forms such as



the electron density at the ortho and para positions is further decreased, which makes nitration take place more readily at the meta positions. On the other hand, consider the trialkylanilinium ion, $ArNR_3^+$, for which resonance in the ground state is negligible. Since the $^+NR_3$ group is found to be 100 per cent meta-orienting, factor (1) would require a large difference between the electron densities at the meta and para positions. However, recent work[20] has shown that there is not a large difference in the charges at these two positions. Consequently, factor (1) does not account for the orientation characteristics of the $^+NR_3$ group. Now, examine the structures of the transition states for reaction at the meta and para positions of $ArNR_3^+$.



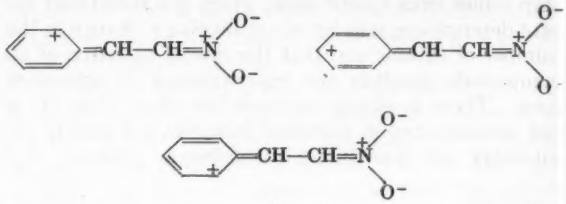
(I)



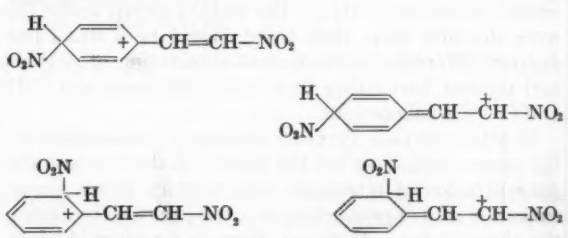
(II)

Calculations[20] of the electrostatic repulsion between the positive charges of (I) and (II) showed that the para-position transition state is destabilized by 10 kg.-cal. more than the meta-position transition state. Such an energy difference could account for the complete meta substitution observed.

As another example, consider the β-substituted styrenes, Ar—CH=CH—G, where G is an NO_2, CHO, COOH, or SO_2Cl group. The electron withdrawing effect of G is transmitted 90 per cent across the double bond, which explains the observed reduction in reactivity of these styrenes with respect to benzene. However, owing to resonance in the ground state of nitrostyrene, for instance, among forms such as



it is expected that substitution would occur at the meta positions as with nitrobenzene. On the contrary, substitution takes place primarily at the ortho and para positions. Again consider the probable structures of the transition states. It is seen that, owing to resonance among forms such as



only the ortho- and para-position transition states are stabilized by resonance involving the side chain. This resonance stabilization of the transition state decreases the respective activation energies to bring about ortho and para substitution. Here again, factor (1) is not able to account for the observed orientation properties and factor (2) is found to be the more important, a point that has been stressed by previous authors.[20, 21]

The third factor which has a marked effect upon orientation of substitution, the steric effect, is that of hindering reaction at the ortho positions. Electrical effects from the substituent are transmitted primarily to the ortho and para positions but only in a small extent to the meta positions, while the steric factor affects only the ortho positions. Consequently, the

[20] ROBERTS, J. D., R. A. CLEMENT, AND G. G. DRYSDALE, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

[21] ROBERTS, J. D., AND A. STREITWIESER, *J. Am. Chem. Soc.*, **74**, 4723 (1952); M. J. S. DEWAR, *ibid.*, **74**, 3357 (1952); F. G. BORDWELL AND K. ROHDE, *ibid.*, **70**, 1191 (1948); G. W. WHELAND, *ibid.*, **64**, 900 (1942); B. PULLMANN, *Bull. soc. chim.* (*France*), **1948**, 533; **1947**, 652; C. A. COULSON AND H. C. LONGUET-HIGGINS, *Proc. Roy. Soc.* (*London*), *A* **192**, 16 (1947); R. DAUDEL AND A. PULLMAN, *J. phys. radium*, **7**, 105 (1946); G. E. K. BRANCH AND M. CALVIN, *loc. cit.*, p. 475.

para/meta ratio of activities should reflect only the difference in electrical influences at these two positions, while the ortho/meta and ortho/para ratios should reflect the combined effects of steric and electrical influences. From the ratios of the respective partial rate factors[22] listed below, it can be seen that the para/meta ratios for methylbenzene are of the same order of magnitude as for the larger alkyl group substituted benzenes, but the ortho/meta and ortho/para ratios for the alkyl benzenes are only one-tenth as large as those of methylbenzene. This shows that spatial interference from the large alkyl groups is hindering ortho-substitution in these compounds.[23]

Ratios of Partial Rate Factors

Propylation	*Ortho/para*	*Ortho/meta*	*Para/meta*
$C_6H_5CH_3$	0.355	1.22	3.44
$C_6H_5CH(CH_3)_2$	0.069	0.16	2.32
Nitration			
$C_6H_5CH_3$	0.724	16.8	23.2
$C_6H_5C(CH_3)_3$	0.073	1.37	18.7

The fourth major factor listed above that affects orientation is the nature of the reagent. One might reason that a highly reactive reagent, such as a carbonium ion in alkylation, does not care much about which molecule it reacts with; it will simply react with the first molecule it encounters. In other words, reaction would tend to take place with benzene about as readily as with many other compounds. In this connection, the ratio of rates of alkylation of toluene to benzene is 2:1, not very large. Furthermore, when the highly reactive reagent reacts with an aromatic molecule, the reagent probably would not be selective about which carbon atom of the aromatic ring it reacted with. That is, there will be little preferential orientation, and it is noteworthy that alkylation of toluene gives 25–30 per cent meta substitution. The purely statistical value is 40 per cent. In the opposite case, a less reactive reagent such as molecular chlorine will be more selective about which type of molecule it will react with. It will choose the molecule of greatest electron density. So it is that the ratio of rates of chlorination of toluene to benzene is 350:1. And, too, the unreactive reagent is particular about which nuclear carbon atom it reacts with, picking the one at which electrons are the most available. In connection with this, less than one per cent meta substitution occurs in the chlorination of toluene. Between these two extremes the ratio of reactivities of toluene to benzene is found to be 24:1 for nitration and 20:1 for bromination by bromine cations. This is an oversimplified description, of course, but one to express the point, as well as to bring out added importance of factor (1) above.

Activity of reagent:	X_3	<	$^+NO_2$, X^+	<	R^+
Per cent meta substitution:	~ 0.1		4–11		25–30

A semiquantitative correlation has been drawn between activity of the reagent and per cent meta substitution, which has been useful in checking the fraction of meta substitution that is expected in certain reactions.[24] The important point is that the nature of the reagent does affect orientation of substitution, probably owing to the relative polarizing powers of the various reagents upon an aromatic molecule. This view has been expressed by several authors.[25]

In conclusion then, electrophilic aromatic substitution apparently takes place by the formation of an intermediate pentadienate cation, ^+ArG, where Ar is an aromatic molecule and G is a portion of the reagent. The steps in the production of this carbonium ion may differ to a small degree for the various types of reactions. The mechanism of nitration is fairly well established and substantiated by considerable experimental data but the mechanism of halogenation is complex and not clearly defined, while the mechanism of alkylation is still uncertain. Concerning orientation of substitution, four factors may be regarded as having strong influences. Then, what is observed experimentally is the result of the combined energy relationships of these four factors with minor alterations from experimental conditions of temperature, solvent, concentrations of reactants, etc.

This topic is one of continued, wide interest, and research is being conducted on its various aspects in laboratories of several countries. It has long been an interesting subject and the story becomes more colorful when the many correlations between orientation of substitution and the physical and chemical properties of aromatic substances are described.

[22] Partial rate factors are integers to represent the relative rates of reaction at the nuclear carbon atoms of a substituted benzene with respect to a carbon atom of benzene.

[23] This steric effect appears to be insignificant in the substitution of the aryl halides because the corresponding ratios for nitration and bromination are as follows:

	Ortho/para	*Ortho/meta*	*Para/meta*
Nitration			
C_6H_5F	0.07	24	348
C_6H_5I	0.32	38	120
Bromination			
C_6H_5F	0.06	64	1070
C_6H_5Br	0.08	133	1730

A steric effect here is obviously lacking.

[24] Brown, H. C., and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

[25] Dennis, S. F., A. S. Powell, and M. J. Astle, *ibid.*, **71**, 1484 (1949); G. W. Wheland and L. Pauling, *ibid.*, **57**, 2086 (1935); B. Pullman, *Bull. soc. chim.* (*France*), **1948**, 533.

A SYNTHETIC DETERGENT: A CASE STUDY FOR APPRECIATIONS IN CHEMISTRY[1]

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THE problem of discussing chemical work in such a fashion as to allow the interested person who has little technical background to appreciate its complex fabric of methods, activities, and results is a difficult and an important one.

A discussion of "what chemistry is" or "what is the nature of chemical work" is often a preface or an introduction to an elementary textbook. It comprises, by tradition, a recital of some of the ways in which the end products of chemical technology have affected our day-to-day activities. These have otherwise been called to the attention of the student and of the educated and intelligent adult, often in a somewhat crude or misleading manner, by radio and newspaper advertising. They have been described more carefully and more entertainingly in radio and television programs of a scientific nature, in popular scientific articles, and in news reports. The applications of research and development in chemistry in relation to the security of the nation and in the production of essential materials of industry and of warfare have been impressed on the public somewhat more vaguely but no less forcefully by the events of the last decade.

[1] Presented in part at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

Such information is certainly important in the development of an appreciation of the importance of chemical work in our material culture, but it actually tells little of the nature of chemistry.

It can be argued, on the other hand, that to know what chemistry is, one must first study elementary principles, and must have some knowledge of descriptive chemistry. A knowledge of chemistry, an understanding of the nature of chemical work, and an appreciation of the role of chemistry in our society are generally recognized aims of the formal work in chemistry for secondary-school students, and for those college courses in chemistry and in physical science which are intended for the nonspecialist. The major emphasis, properly, has been on the first of these aims—a knowledge of chemistry.

There is a large and important area of understandings and appreciations not developed by studying facts and principles organized in logical fashion, and not included in the popular appreciation of the wonders of modern chemistry. The recognition of this area used to be made, almost superficially, by brief descriptions of the essentials of the scientific method at the beginning of textbooks of chemistry. Such descriptions scarcely illustrated the method. More

Outline of Topics and of Concepts in Order of Development

Fundamental research	
Selected topics in the chemistry of benzene	
Isolation	Discovery of a new material and its characterization
Composition (quantitative analysis, molecular composition)	Qualitative and quantitative nature of descriptive chemistry, molecular theory
Valence theory and the structure of benzene	Need for theory of structure; unifying concepts from inductive reasoning
Selected reactions	Investigations of behavior of a new compound
The Friedel-Crafts hydrocarbon synthesis	
Discovery	"Accidental" discovery of a new reaction
Applications	Principle of generality in chemical behavior
Soap	
History	A "practical art" and its empirical development
Structure	Improvements in manufacture and use follow theory
Molecular sizes and shapes	
Experimental techniques	Importance of methods and tools for investigation; new insights through new experimental techniques
Monomolecular films and molecular architecture	Submicroscopic properties correlated with theory and with macroscopic behavior
Mechanism of detergent action	
Orientation at surfaces, emulsification	Physical phenomena explained by chemical forces
Developmental research	
Synthetic materials	Synthesis to imitate the structure of a natural product; specific variations and improvements
Synthesis of a detergent	Conceptual development and practice requiring, as background, all work previously described
Commercial chemical development	Engineering, control, testing, research, improvements, new applications

recently, these understandings and appreciations have received increasing attention in the organization of science courses at the college level for nonscience students.[2] A direct attack on the problem of organization of material for a college course which will contribute to "understanding science" by Conant[3] and by others[4] has had an important influence in teaching chemistry. That approach is a rigorous one, requiring extensive, carefully selected readings in the earlier scientific literature.

It should be possible to discuss some phases of chemical work in a way less rigorous than the historical approach of Conant, yet less superficial than that of the popular articles describing chemical developments. The illustration outlined in the table is an attempt to lead toward the understandings and appreciations so important for the layman. In developing it, it is necessary to use some technical terms, descriptions of apparatus, structural formulas; yet it is believed that this can be done so that it will be understandable to one who knows little chemistry.

The plan of attack in this illustration is to select a chemical product of some interest—a synthetic detergent which is one of the relatively new "soap substitutes" for household use—and to describe its chemical history. The product chosen is a prosaic one; a new drug, a synthetic rubber, a new fiber might equally well serve as illustration. One looks first at some of the earlier chemical work, research of the period 1825–1925, which was directed toward finding out the structure of some simple substances. It should be possible to develop in this way an appreciation of some of the different types of work in fundamental chemical research. The second type of work, the development of a product of some importance, follows logically in the discussion. In this way, as part of a continuing development, a series of separate topics is presented. Each of these illustrates some facet of chemical work which contributes to the over-all picture of the nature of chemistry; and each, at the same time, is a part of the story of the development of a synthetic detergent.[5]

Within the framework of a topic such as this, there is opportunity to illustrate a number of points of some importance for popular understanding of chemical work and appreciation of the varied nature of its motivations, techniques, and results.

The distinction between so-called pure research and applied research, which may well be made on the basis of motivation, is illustrated by contrasting the early work on structure, work undertaken primarily to satisfy a refined curiosity or to establish order and pattern in a group of otherwise chaotic observations, with the purposeful synthesis of materials of utility or of potential commercial importance, and with the scientific examination and improvement of processes of commercial importance. One can profitably use such an illustration to explore the differences between science and technology; to draw the fine line in these examples is to invite argument, but the broad distinctions are clear.

A detailed examination of several of the developments outlined would be necessary to convey adequately the varied approaches in chemical research problems and the wide differences in the fundamental nature of each of these. There is included, for example, a typical instance of the isolation of a new natural product by careful observation, one of determination of composition based on analytical methods, one of pioneering hypothesis on fundamental principles of structure. The discovery of properties and of new compounds by what now appears to be random experimentation, the future importance of general synthetic methods so discovered, and the development of a completely new tool to measure new properties are further examples.

A general point of great importance is the complicated nature of the interrelation of work in various fields and the dependence of scientific work, at any time, on the body of accumulated factual information, techniques, and theories. Main threads of the pattern serve to illustrate this; to trace back each contribution would involve a tremendous amount of past work. The complete dependence of applied or developmental work on basic research, and the dependence of both on the exchange, publication, and abstracting of scientific information are obvious corollaries.

An appreciation of the varied types of activities in chemical work is important for anyone considering chemistry as a vocation. Such variety is obviously demonstrated in the examples chosen, but a detailed development would be required if one were primarily interested in such aspects.

The outline presented in the table is the essential instructional device, and it can be given body and internal relation in a number of ways. Presenting the material in a series of short lectures is probably the least satisfactory way, from the point of view of the student; much more is accomplished if he can fill in the details for himself by reading and study. Ideally, then, such material ought to be presented in the form of original sources and in detailed descriptive commentary which students might study, report on, and discuss. If carefully enough done, this might be as satisfactory a way as any to introduce organic chemistry in general college chemistry. That such material is not readily available and indeed is somewhat difficult to organize, is a major limitation, for any use, of the point of approach suggested. Material of this sort may well be of value, however, even if the treatment is incomplete and methods of presentation are not ideal, in arousing interest in chemistry and in bringing important appreciations to those for whom chemistry is a part of our culture.

[2] McGrath, E. J., "Science in General Education," Wm. C. Brown Company, Dubuque, Iowa, 1948; Entrikin, J. B., J. Chem. Educ., 28, 274 (1951).

[3] Conant, J. B., "On Understanding Science," Yale University Press, New Haven, 1947.

[4] Nash, L. K., J. Chem. Educ., 28, 146 (1951).

[5] See, for example, Bunce, Stanley C., *School Sci. and Math.*, 54, 637 (1954).

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

GRAM EQUIVALENT WEIGHTS[1]

WILLIAM B. MELDRUM
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THE purpose of this paper is to review very briefly the subject of equivalent weights and the more directly applicable gram equivalents and to offer a general method by which they may be deduced from chemical equations.

The concept of equivalent weights and of the closely related gram equivalents is of fundamental importance in chemistry. It is one with which the chemistry student has to wrestle in several connections during his college career. He meets it first in the general chemistry course, where equivalent weights are studied as a basis for atomic weights. Their importance in this application may be realized from the fact that of the presently accepted atomic weight values all but a very few, perhaps 15, were determined from gram equivalents. They are next met in the study of Faraday's famous second law of electrolysis, which relates the quantitative effects at the electrodes to the equivalent weights of the substances changed. On the basis of this law we define the *faraday* as the quantity of electricity that brings about one gram equivalent change at an electrode. Then, in quantitative analysis, the student finds that the gram equivalents of substances, both elementary and compound, are virtually indispensable because of two applications. First, in order to calculate what weight of a reagent will be required to prepare a solution of specified normality, the gram equivalent of the reagent must be known. For example, if one wants to prepare an approximately 0.1 *N* solution of potassium permanganate to use for titrations in acidic solution, he must know that the gram equivalent is one-fifth of a mole, or 31.61 g. Second, the gram equivalent of the constituent being determined in a volumetric analysis must be known in order to calculate the per cent of it in a given sample from the results of a titration and the normality of the reagent solution. For example, if one wants to calculate the per cent of nitrogen in a sample from the data of a Kjeldahl determination, he must know that the gram equivalent of nitrogen is 14.008 g. This, together with the volume of standard acid solution neutralized by the ammonia distilled over, its normality, and the weight of the sample, leads to the per cent of nitrogen. These various applications, all of them highly important both in teaching and practicing the science, furnish sufficient reason why the student should have a clear knowledge of equivalent weights and gram equivalents.

It is unfortunate to the teaching of chemistry that the treatment of this subject in most of our textbooks is so meager and so confusing. Nor is it free from "false doctrine," the use of stop-gap information that has to be relearned differently later in the student's chemistry career. It seems safe to say that no topic of comparable importance receives such inadequate discussion and attention.

The experienced analyst is not greatly concerned over the lack of a general method of deducing equivalent weights. But pity the poor student! In the general chemistry course he learns some simple rule, such as "the equivalent weight of an element is the atomic weight divided by the valence." Later, in quantitative analysis, he meets with so many exceptions to this rule that he realizes that it is virtually worthless. In the general chemistry course, again, he may be taught that the standard for equivalent weights is 1.008 parts of hydrogen by weight, a standard given in eight out of eleven books examined by the writer. Later, in some more discriminating study, perhaps in the physical chemistry course, he finds that oxygen = 8.000 is the accepted standard. He learns that the equivalent weight of an acid is the molecular weight divided by the number of replaceable hydrogens in the molecule. Later, he finds that if the number of theo-

[1] The method of deducing equivalent weights and gram equivalents to be described was discussed at the 15th Summer Conference of the New England Association of Chemistry Teachers held at Bowdoin College in 1953. In part, the paper parallels the treatment of the subject in a book on quantitative analysis by Albert Frederick Daggett, of the University of New Hampshire, and the writer, to be published shortly by D. C. Heath and Company.

retically replaceable hydrogens is greater than unity, the rule is valid only under certain conditions. Further, he learns that the equivalent weight of a salt is the formula weight divided by the number of cation valences or, perhaps, it is the weight of the salt "that contains one gram equivalent of the metal or positive group." Later, he finds that such a rule as this is true only sometimes and he is in no position to predict when it will hold and when it won't. The fact is that the so-called rules which the student finds in many textbooks are of little use to him in practice and render the subject confusing to him. Sometimes, they are definitely incorrect.

Some textbook authors have tried to bring some degree of order out of this existing chaos and to them due credit must be accorded. So far, however, no treatment has been satisfactorily comprehensive and really helpful to the student. This unfortunate situation has caused the writer concern for a long time, especially in his teaching of quantitative analysis, where the logical deduction of gram equivalents becomes a matter of direct interest. In an effort to integrate our knowledge of the subject he has been led to prepare this summary on gram equivalents and to suggest a way in which they may safely be deduced from chemical equations. Students have handled this method in a very gratifying manner.

The fundamental definition of equivalent weight is this: The equivalent weight of a substance is the number of parts by weight of it which combine with or are otherwise chemically equivalent to 8.000 parts by weight of oxygen. In laboratory practice we customarily deal with weights expressed in grams, and so the more precise quantity of gram equivalent is more directly useful. We may define this quantity thus: The gram equivalent of a substance is the number of grams of the substance which are chemically equivalent to 8.000 g. of oxygen. The term "chemically equivalent" need not be defined precisely; its meaning is well understood by any thinking student. It is, however, of interest to recall that "equivalent" was first used in this chemical sense by the great scientist Henry Cavendish, in 1767, with reference to the quantities of potash and lime required to neutralize the same quantity of an acid.

Beyond this fundamental definition it is essential to keep in mind that the gram equivalent of any substance is a quantity based primarily upon experiment. It may not be the same for all of the reactions of the substance; in fact, it is a common experience to find several different gram equivalents for the same element or compound. By way of illustration of this we may cite the following cases:

(1) The gram equivalent of iron in its reaction with dilute hydrochloric or sulfuric acid,

$$Fe + 2H_3O^+ \rightarrow Fe^{++} + H_2\uparrow + 2H_2O$$

or when it is deposited from a ferrous sulfate solution by the electric current,

$$Fe^{++} + 2\epsilon \rightarrow Fe\downarrow$$

is one-half the gram atom, 27.93 g. In the reaction of iron with chlorine to form ferric chloride,

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

it is one-third the gram atom, 18.62 g. But in the reduction of ferric ion to ferrous ion by a reducing agent like stannous chloride,

$$2Fe^{+3} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{+4}$$

or in the oxidation of ferrous ion to ferric ion, when, for example, bromine is added to a solution of ferrous chloride,

$$Fe^{++} \rightarrow Fe^{+3} + 1\epsilon$$

it is the same as the gram atom, 55.85 g.

(2) The gram equivalent of ferrous ammonium sulfate hexahydrate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, when the acidified solution of the salt is oxidized by a ceric or permanganate or some other oxidizing solution, is equal to the gram formula weight, 392.15 g. Here the oxidation reaction is merely

$$Fe^{++} \rightarrow Fe^{+3} + 1\epsilon$$

If the ferrous ammonium sulfate solution reacts with potassium ferrocyanide,

$$2Fe^{++} + Fe(CN)_6^{-4} \rightarrow Fe_2Fe(CN)_6\downarrow$$

or is electrolyzed to deposit iron,

$$Fe^{++} + 2\epsilon \rightarrow Fe$$

the gram equivalent is one-half the gram formula weight, 196.08 g. If the solution is used to precipitate barium sulfate by reaction with barium chloride solution,

$$SO_4^{--} + Ba^{++} \rightarrow BaSO_4\downarrow$$

the gram equivalent is one-quarter the gram formula weight, 98.04 g.

The deduction of the gram equivalents of elements when they react to form binary compounds presents no difficulty. We simply note the weights of the elements which combine with 8.000 g. of oxygen or with the known gram equivalent of some other element, *e. g.*, 1.008 g. of hydrogen, which itself combines with oxygen. Attention must be paid, of course, to the valence states of the reacting elements as indicated by the formulas of the products.

The real difficulty comes in dealing with compounds. Compounds, more so than elements, take part in several different types of reactions. What we are seeking is a rule for deducing gram equivalents that will cover all of these types. This we think we have worked out. As a "working definition," which is readily derivable from the fundamental definition cited above and which seems to be applicable in all ordinary cases, we offer this: The gram equivalent of a substance taking part in a given reaction is the number of

grams of the substance associated with the transfer of n electrons or protons or with the neutralization of n negative or positive charges, where n is Avogadro's number, 6.02×10^{23}.

The relation between Avogadro's number and the gram equivalent change is important to our present proposition and may be recalled briefly as follows:

The *faraday*, which is approximately 96,500 coulombs, is the quantity of electricity which will bring about one gram equivalent change at each electrode when a direct current passes through an electrolytic cell. If the current is passed through a solution of potassium nitrate between platinum electrodes, one faraday deposits 8.000 g. of oxygen at the anode and 1.008 g. of hydrogen at the cathode. Thus we see that one faraday is equivalent to 1.008 g. of hydrogen, *i. e.*, to a half mole of hydrogen, or 3.01×10^{23} hydrogen molecules, or 6.02×10^{23} hydrogen atoms, and to 6.02×10^{23} hydrogen ions discharged. When 6.02×10^{23} hydrogen ions are discharged, the same number of electrons is transferred to them. Hence 1 faraday of electricity equals n electrons.

When we write an equation for an oxidation reaction by showing the removal of electrons,

$$2I^- \rightarrow I_2 + 2e$$

or for a reduction reaction showing the gain of electrons

$$Fe^{+3} + 1e \rightarrow Fe^{++}$$

we are representing the loss or the gain of one electron per ion. But if we take, as we do, the formula of the ion to represent one mole, then each "e" in the equation stands for n electrons.

Furthermore, because each negative charge on an ion represents an excess, and each positive charge a deficiency of one electron per ion, they likewise represent an excess, or deficiency, of n electrons per mole of the ion. According to our "working definition" the quantity of the ion neutralized by n charges of the opposite sign will be its gram equivalent. Thus we bridge the gap between oxidation-reduction reactions in which there is a transfer of electrons and other types of reactions where a neutralization of charges is involved.

In order to realize how our "working definition" may be applied to the several types of reactions, let us consider briefly some representative cases.

(1) *Oxidation-Reduction (Redox) Reactions.* What is the gram equivalent of potassium permanganate and of sodium sulfite when they react together in acidic solution? The over-all equation for the reaction is

$$5SO_3^{--} + 2MnO_4^- + 6H_3O^+ \rightarrow 5SO_4^{--} + 2Mn^{++} + 9H_2O$$

If we break this into the two step equations (corresponding to half-cell reactions), we have

$$\textit{Oxidation:}\ SO_3^{--} + 3H_2O \rightarrow SO_4^{--} + 2H_3O^+ + 2e$$
$$\textit{Reduction:}\ MnO_4^- + 8H_3O^+ + 5e \rightarrow Mn^{++} + 12H_2O$$

Each mole of sulfite ion loses $2n$ electrons; hence the gram equivalent of sulfite ion and of the sodium sulfite used as solute will be one-half the mole, *i. e.*, 63.03 g. of sodium sulfite. Each mole of permanganate takes on $5n$ electrons; the gram equivalent of permanganate ion and of potassium permanganate will be one-fifth of the mole, *i. e.*, 31.61 g.

What is the gram equivalent of potassium permanganate and of manganous sulfate monohydrate when the following reaction occurs in neutral solution?

$$3Mn^{++} + 2MnO_4^- + 6H_2O \rightarrow 5MnO_2\downarrow + 4H_3O^+$$

Writing the two step equations, we have

$$\textit{Oxidation:}\ Mn^{++} + 6H_2O \rightarrow MnO_2\downarrow + 4H_3O^+ + 2e$$
$$\textit{Reduction:}\ MnO_4^- + 4H_3O^+ + 3e \rightarrow MnO_2\downarrow + 6H_2O$$

One mole of the salt $MnSO_4 \cdot H_2O$ yields one mole of manganous ion, Mn^{++}, which oxidizes to manganese dioxide and loses $2n$ electrons. Hence the gram equivalent is one-half of the mole, or 84.51 g. One mole of potassium permanganate yields one mole of permanganate ion, MnO_4^-, which upon reduction to manganese dioxide takes on $3n$ electrons. Hence the gram equivalent is one-third of the mole, or 52.68 g.

(2) *Acid-Base (Neutralization) Reactions.* In an acid-base reaction electrons are not transferred. However, protons, H^+, are transferred from the acid to the base and it is upon the number of these that the calculation of the gram equivalent is based. In the reaction between solutions of sodium hydroxide and hydrochloric acid, for example,

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

one proton is transferred from the hydrogen ion to the hydroxyl ion. If we consider that the equation represents molar quantities, n protons are transferred from one mole of hydrogen ion to one mole of hydroxyl ion. Hence we deduce that the gram equivalent of hydrochloric acid is equal to the mole and that of sodium hydroxide is also equal to the mole, 36.46 g. and 40.01 g., respectively.

What is the gram equivalent of sodium carbonate, Na_2CO_3, when it is used to standardize a solution of sulfuric acid? What is the gram equivalent of sulfuric acid? In the titration it is customary to use methyl orange, or some other substance of similar pH range, as indicator. The indicator color changes from the clear yellow of the basic solution toward red at a pH of about 4.4 as acid is added. This indicates the end point of the reaction

$$2H_3O^+ + CO_3^{--} \rightarrow H_2CO_3 + 2H_2O$$

It is obvious in this case that one mole of the sodium carbonate yields one mole of carbonate ion and that, in the reaction, $2n$ protons transfer from the hydrogen ion to the carbonate to form carbonic acid and water. Thus the gram equivalent of sodium carbonate must be one-half of the mole, or 53.00 g., and that of the sulfuric acid is also one-half of the mole, or 49.04 g.

All acids and bases may be treated in this way. It should be emphasized that the number of protons actually transferred in the reaction determines the equivalent weight.

(3) *Precipitation Reactions.* This type of reaction usually involves the transfer of neither electrons nor protons. Instead, ions combine to yield an ionic compound of low solubility. The ions are not discharged; they merely go to form a crystal lattice and are neutralized only statically. The gram equivalent is calculated from the number of charges neutralized in this way.

For the reaction between sodium chloride and silver nitrate solutions we write

$$Ag^+ + Cl^- \rightarrow Ag^+Cl^- \downarrow$$

which tells us that the positive charge on the silver ion and the negative charge on the chloride ion neutralize each other statically when the silver chloride is precipitated. If we consider *moles* of reacting ions, then we see that n positive charges and n negative charges are neutralized. Hence the gram equivalent of silver nitrate and the gram equivalent of sodium chloride are each equal to the mole, *i. e.*, to 169.89 g. and 58.46 g., respectively.

Let us consider a less obvious case. Potassium ferrocyanide precipitates the zinc from a zinc sulfate solution according to the equation

$$3Zn^{++} + 2K^+ + 2Fe(CN)_6^{-4} \rightarrow Zn_3K_2[Fe(CN)_6]_2 \downarrow$$

When three moles of zinc ion, Zn^{++}, react, $6n$ charges are neutralized; hence the gram equivalent of zinc will be one-half of the gram atom, or 32.69 g. In order to neutralize the $6n$ charges of the three moles of zinc ion, two moles of ferrocyanide ion must react; hence the gram equivalent of the potassium ferrocyanide is one-third of a mole, or 122.78 g. In contrast to this, the gram equivalent of sodium ferrocyanide, $Na_4Fe(CN)_6$, is *one-quarter* of the mole. With it the reaction of a zinc salt is

$$2Zn^{++} + Fe(CN)_6^{-4} \rightarrow Zn_2Fe(CN)_6 \downarrow$$

This rather curious fact emphasizes further that the gram equivalent must be deduced from the reaction, not merely from the formula of the substance.

(4) *Complex-ion Formation Reactions.* The calculation of the gram equivalent of a substance taking part in a reaction involving the formation of complex ions is not a frequent need in analytical chemistry but it is required in some important cases. One case in which it may fruitfully be applied is in the well-known von Liebig method for determining the potassium cyanide content in the crude material used as insecticide, for case-hardening, and for electrolytic purposes. In the determination, the dissolved sample of the cyanide is titrated with standard silver nitrate solution until a white precipitate just begins to form. The main reaction is

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

and the production of the precipitate indicates the beginning of the reaction

$$Ag(CN)_2^- + Ag^+ \rightarrow 2AgCN \downarrow$$

The per cent of potassium cyanide is calculated by the usual expression,

$$\%KCN = \frac{(\text{vol. } AgNO_3 \times n)}{1000} \times \frac{(\text{g. eq. KCN})}{(\text{wt. sample})} \times 100$$

What is the gram equivalent of potassium cyanide? When one mole of silver ion changes into the complex ion according to the first equation, n charges are neutralized. These n charges that are neutralized are associated with two moles of cyanide ion. Hence the gram equivalent of potassium cyanide must be twice the gram formula weight, or 130.24 g.

SUMMARY

This general method for deducing gram equivalents has been found very useful by application in numerous cases. One cannot claim perfection for it, however, for one case has been found to which it cannot be fruitfully applied. This is in the cyanide method for determining copper. The key reaction in this process is in the titration of ammoniacal cupric solution with potassium cyanide solution; at the end point the purple-blue of the cupric-tetraamino complex ion gives place to the light brown cupro-cyanide complex ion. The reaction is complicated and involves reduction of the copper from cupric to cuprous and at the same time the formation of the cupro-cyanide complex ion. The overlapping of these two processes invalidates the application of the method for deducing the gram equivalent. Other cases may also be found in which the method is not valid. Even though the method may not be the last word, nevertheless it is an attempt to clarify a situation which is, for the most part, vague and baffling to the student.

ACKNOWLEDGMENT

In conclusion, the writer wishes to express his appreciation of suggestions and encouragement received from Dr. A. F. Daggett, of the University of New Hampshire, and from his colleagues at Haverford, Dr. T. O. Jones and Dr. O. T. Benfey.

To the Editor:

The recent article by D. D. DeFord (THIS JOURNAL, **31**, 460 (1954)) mentions that solubility products are frequently not accurately known, and that many calculations in quantitative analysis may therefore be of little value.

I think it may be interesting to mention one notable example, inasmuch as it affects the validity of that classic calculation, the determination of the exact chromate ion concentration necessary to make the endpoint in Mohr's method coincide with the equivalence point. This calculation requires the use of the solubility products of both silver chloride and silver chromate, quantities which one would imagine to be known to a high degree of accuracy.

In five leading texts of quantitative analysis published between 1943 and 1954 one finds that the solubility products of silver chromate cover the range from 0.57 to 9.0×10^{-12} and even the solubility product of silver chloride ranges from 1.0 to 1.7×10^{-10}. The extreme range of "correct" chromate ion concentrations using these values would be 0.003 to 0.09 molar.

In each of the texts the calculation is made, and then the observation that this is not the "practical" chromate ion concentration to use, only the theoretical. However, even the practical values suggested ranged from 0.002 to 0.01 molar, which hardly indicates perfect unanimity.

J. P. PHILLIPS

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To the Editor:

With reference to the paper "The use of a radio-frequency oscillator in student analysis," by James L. Hall and his associates which appeared in THIS JOURNAL, **31**, 54–9 (1954), as the originator of radio-frequency chemical analysis in 1936 and the first to apply r.-f. for that purpose by the application of external electrodes in 1944, I should like to congratulate the authors on their paper. I am, however, disappointed not to have received credit in their reference list for my own work which opened the door to this new analytical field.

My work is described in detail with the dates and titles of my own and other workers' publications up to the time of printing. My first edition, "Conductimetric Analysis at Radio-frequency," was published in England by Chapman and Hall in 1950, and my American edition was published by the Chemical Publishing Co. of New York in 1952.

G. G. BLAKE

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To the Editor:

Perhaps other teachers of chemistry have, like me, had scant certainty of what becomes of the cryolite so essential in the reduction of aluminum from its ore. Textbooks generally seem to consider it of little importance. Statements about it often leave the implication that since "theoretically it lasts forever" no further attention to its performance is in order.

Schlesinger,[1] in a footnote, says the "quantity [of cryolite] used up is relatively small." He further states that there is now an artificial cryolite available to supplement the limited natural mineral supply obtainable only from Greenland.

The facts appear to be that not only does the cryolite not "last forever" but that the quantity needed by huge modern reduction plants is by no means small. For every ton of free metal produced, it is reliably stated[2] that one-tenth of a ton of cryolite is lost. One of the Reynolds plants[3] is currently producing 100 million pounds of aluminum metal per year. Obviously 10 million pounds of cryolite is not a small quantity. Its loss is something to be reduced.

Another aspect of cryolite's place in the company's concern is its part in the adverse publicity of litigations that involve thousands of dollars. One such suit for damages alleged to have been entailed by a dairy herd was recently reduced by the court from $42,000 to $14,000 "in view of the corrective measures which have been taken" by the defendant. Of the last half of the period covered by the suit the judge said, "The defendant had installed fume controls which have proven effective."

Here, as in many other industrial controls of wastes, the "corrective processing" has both reduced annoying litigation and at the same time salvaged a necessary processing chemical. By the combination of these captured gases and the scrubbings of reclaimed cryolite from the spent reduction cells, replacement for the 10 million pounds of lost cryolite is produced locally, an accomplishment, certainly, for economy, and one that is of much interest to the public as well.

I submit the above as of interest to chemistry teachers. It might also merit a "footnote" rating for the students of the course.

B. CLIFFORD HENDRICKS

LONGVIEW, WASHINGTON

[1] "General Chemistry," Longmans, Green & Co., New York, 1937, p. 179.
[2] "Encyclopedia Britannica," 1951, Vol. I, p. 714.
[3] In Longview, Washington.

● THE STRUCTURES AND REACTIONS OF THE AROMATIC COMPOUNDS

G. M. Badger, Reader in Chemistry in the University of Adelaide. Cambridge University Press, New York, 1954. xii + 456 pp. Many figs. and tables. 14.5 × 22 cm. $11.50.

EVER since Kekulé made his classic suggestion for the structure of benzene a tremendous volume of theoretical and experimental evidence has been amassed in an attempt to ascertain the actual structure of benzene and its close relatives, the more common aromatic hydrocarbons. Now, after nearly one hundred years, our conception of the structure of benzene is more rational, and undoubtedly more nearly correct, than the proposal of Kekulé. Of all the structural problems in organic chemistry, the structures of the aromatic compounds are perhaps the most fascinating. It seems quite reasonable that an organic chemist should be sufficiently fascinated to survey the field of structural aromatic chemistry and to then compile this information in textual form.

Dr. Badger notes in the preface of his book that "specialization has many dangers," and that often "it becomes more and more difficult to see the wood for the trees." He seems to be an excellent "woodsman." He is aware that the "trees" differ in size, variety, and individual significance within the "wood." He also appears quite able to recognize each "tree's" current degree of maturity. Most readers will agree that he has written this volume in a remarkably dispassionate manner.

The organization of the material follows a commendable pedagogical pattern. In the major, individual sections the problem is stated first, then the experimental evidence, and finally the current, theoretical solution. Most of the book is descriptive, but many examples are given in certain sections to clarify the over-all picture. Ample references are made to the original literature.

Because the title of the book may be misleading to some potential readers, it should be noted that the author has placed definite boundaries on his material. Certain "less important substitution reactions" have not been included. Synthetic methods have been omitted, except for a few which involve direct substitution or addition to an aromatic nucleus. Very few side reactions are discussed, and then usually to explain the effects produced by nuclear substituents or to indicate the nature of inductive and mesomeric effects. Much of the more recent work on tropolone and on the Friedel-Crafts reaction could not be included, unfortunately, because the reports were published after the author had completed the text. For the most part, references to the literature are not later than the middle of 1951. In essence, the book is mainly concerned with the apparent electronic structures of the common, aromatic nuclei and the reactions which directly involve these aromatic nuclei.

The problematical existence of the so-called aromatic "double" bond is treated quite aptly. The discussion of the structure of naphthalene relative to the evidence for a "double" bond at the 1–2 position and a "single" bond at the 2–3 position is exceptionally good. Students who read this book will surely be impressed by the manifold evidence for the present concept of the exceptional electronic mobility of the so-called hybrid state of an aromatic nucleus. Students will also appreciate the fact that the electrons in the hybrid may be localized, more or less, by the presence of another substance, and especially at the instant before a chemical reaction. With this realization in mind, the thoughtful student should not be unduly confounded when he is told that both nucleophilic and electrophilic substitution on naphthalene occur most frequently at the 1-position.

The chapter titles indicate, at least partially, the scope of the book: The Benzene Problem; Some Properties of Aromatic Compounds; Addition Reactions of Aromatic Compounds; The Aromatic "Double Bond"; The Effects of Substituents; Aromatic Substitution Reactions; The Diels-Alder Reaction; Photo-Oxidation and Photo-Dimerization; Absorption and Fluorescence Spectra of Aromatic Compounds; Optical Activity in Aromatic Compounds.

Once in a while the text gives the impression that the author has attempted to compress a field too large into a space too small. For the most part, however, the author is quite successful in his rather courageous venture in writing such a book. There are a few occasional statements which, because of brevity, may be somewhat misleading. One appears on page 250: "Benzene, chlorobenzene, toluene, and naphthalene . . . are not methylated under the same conditions but give the normal direct oxidation product." The text appears to be almost entirely free of typographical errors.

This book merits the attention of all teachers of organic chemistry. Advanced undergraduate and graduate students will find it extremely informative and lucid. The book will surely be an invaluable addition to every library.

DONALD C. GREGG

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● INTRODUCTION TO CHEMISTRY

R. T. Sanderson, Professor of Inorganic Chemistry, State University of Iowa. John Wiley & Sons, Inc., New York, 1954. x + 542 pp. 61 figs. 24 tables. 15 × 22 cm. $5.50.

THE number of general-chemistry texts available increases yearly. Not only are most of the better-known texts appearing as revisions, but also an increasingly large number of first editions are on the market.

The majority of recent texts are characterized by the inclusion of large amounts of fundamental material regarding nuclear, atomic, and molecular structure. Many of these texts also contain sections dealing with metallurgy, electrochemistry, organic chemistry, and the chemistry of macromolecules. In fact, they are compendia of the science, chemistry. Such texts are in most cases excellent for students who have had above-average training in secondary-school chemistry or are in a class screened by prerequisites or placement tests. Such texts are also valuable as references during the students' college careers. However, the vast amount and, in some cases, complexity of the subject matter in these texts often frustrates the students and makes a "tough" subject appear tougher.

This text is not one of the aforementioned type. It is significant in its simplicity of style, completeness of fundamental material, and candor in omission of most of the material which probably would not be covered in the elementary course. The author's avowed purpose was to write a text "... long on explanation and short on purely descriptive chemistry." He states: "I see no reason why the lecture cannot be supplementary to the textbook rather than the textbook supplementary to the lectures. If the textbook contains only what the students should learn then they can study it at leisure and with confidence." For those teachers who subscribe to such a philosophy, this text should prove to be a happy choice.

From the first chapter to the last this book is written in a readable style which should capture the attention of students and make them forget it is a text.

Equations, which are extremely scarce in the first two hundred and fifty pages, are for the most part written in ionic form. Clear line drawings and diagrams are liberally used to illustrate structural formulas and reactions.

A superficial examination of this text leaves one with the opinion that it is "too simple." A more thorough perusal of important topics dispells this attitude. The text should be satisfactory for science majors, although its greatest use will probably be found in the terminal course.

The chapters dealing with metals, the chemistry of carbon and silicon, and nuclear changes and nuclear energy are so brief that they serve only to illustrate that such fields of chemistry are existent. One of the undesirable features of the text is the scarcity of exercises at the end of chapters. Many chapters (*e. g.*, Solubility and Solutions, Introduction to Chemical Equilibrium and Ionic Equilibria) have no exercises or problems.

The book is printed in large, clear type with adequate margins and spacing on a dull finish paper. These are valuable features which reduce eyestrain.

WILLIAM B. COOK

BAYLOR UNIVERSITY
WACO, TEXAS

● TOBACCO DICTIONARY

Edited by *Raymond Jahn.* The Philosophical Library, New York, 1954. xi + 199 pp. Illustrated. 14.5 × 22 cm. $5.

THIS compilation contains much to interest the dealer, grower, smoker, and idly curious person. Types of tobacco, cigar terms, slang expressions, pipe shapes, and personages associated with tobacco in one way or another are among the items included. The value of this work as a reference would be considerably enhanced by a more critical treatment of the botanical status of tobacco and plants in general (it is never quite plain whether *Nicotiana tabacum* is considered a species or a variety), more complete references to insect pests and insecticides (and chemicals in general; "Urea. A chemical sold as Uramon. . ." is hardly an adequate description), and more illustrations. These are primarily matters of degree, however, as there seem to be few omissions in the terms listed.

JOEL W. HEDGPETH

SCRIPPS INSTITUTION OF OCEANOGRAPHY
LA JOLLA, CALIFORNIA

● PROGRESS IN THE CHEMISTRY OF FATS AND OTHER LIPIDS. VOLUME 2

Edited by *R. T. Holman* and *W. O. Lundberg,* University of Minnesota, and *T. Malkin,* University of Bristol. Academic Press, Inc., New York, 1954. 347 pp. Many figs. and tables. 16 × 24.5 cm. $9.80.

THE present book is Volume 2 of a projected series of digests of recent advances in the chemistry and biology of lipid materials. It is anticipated that in the future new volumes will be published periodically, possibly yearly. There are seven chapters in this volume, each of which is essentially a monograph by a specialist in some specific area.

The book was written neither for the beginning student of lipids nor for the casual reader, but rather for graduate students and research workers for whom it should prove to be a source of useful information and a basis for new ideas. The authors have attempted to present in detail highly technical material, controversial issues which arise from different experimental techniques, and new methods or procedures. A complete survey of the literature in each area is indicated by the extensive bibliography at the end of each chapter. References to articles published in 1953 are included.

In the first chapter, T. Malkin discusses polymorphism of glycerides. Following this is a monograph by R. T. Holman, entitled "Autoxidation of fats and related substances." Chapter 3 is a comprehensive survey by H. Deuel of the nutritional values of various fats. The surface properties of fatty acids and allied substances by D. G. Dervichian, and an interesting discussion by H. Schlenk entitled "Urea inclusion compounds of fatty acids," comprise the next two chapters. Chapters 6 and 7 are concerned with methods for separating and identifying lipid materials. The use of infrared absorption spectroscopy by D. H. Wheeler and fractionation using countercurrent extraction are discussed in these two monographs.

Stimulating discussions appear in each of these chapters. For example, the use of urea for fractionating mixtures of saturated and unsaturated fatty acids is treated in Chapter 5. A proposed mechanism for the development of oxidative rancidity in lipids, and the influence of dietary fat on the utilization of dietary protein and carbohydrate in metabolism are presented in Chapters 2 and 3, respectively. It is, of course, impossible to elaborate on all the points of interest in each chapter but the discussions mentioned above indicate the wide use of the book for advanced students of lipid nutrition and chemistry.

R. U. BYERRUM

MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

● METHODEN DER ORGANISCHEN CHEMIE. BAND VII, TEIL 1: SAUERSTOFFVERBINDUNGEN II, ALDEHYDE

Edited by *Eugen Müller,* Tübingen. Georg Thieme Verlag, Stuttgart, Germany, 195 . xxiii + 556 pp. 17 × 26.5 cm. $19.50.

PYTHAGORAS, the square-on-the-hypotenuse man of antiquity, is reported by Hermippus to have prepared a deep underground lodging and enjoined upon his mother to mark down every dot and tiddle which transpired, even to the very hour, and to drop the notes down to him. She did. Afterwards, he crawled out of ground, looking like a refugee from a morgue, and proceeded at once to the assembly, where he declared in a loud voice that he had been in Hades and had seen everything, and gave an accurate account of all that had happened. The assembly men were so dumbfounded that they regarded him as divine; they wept and wailed, some even going so far as to send their wives to him to learn his doctrines. Now this may be the "ingenious device" for which mathematicians are eternally seeking. We hope not. One thing is certain, however: this is not a good way to obtain current information, especially of aldehydes, since few mothers have any significant command of the subject and most chemists have no desire to sit in dark caves. A more reliable technique is to search the elegant and exhaustive "Methoden der organischen Chemie."

This great work is divided into two parts: the preparation of aldehydes and their reactions. The section dealing with the synthesis of aldehydes (400 pages) is very complete. It describes in detail methods for the direct introduction of the CHO group; the union of organic residues which contain aldehyde groups; techniques which involve oxidation of groups such as the methyl, primary alcohol, ether, etc.; conversion of certain heterocyclic nitro, and other substances into aldehydes; the transformation of acids and their derivatives into aldehydes; production of aldehydes by degradation reactions; and transformations of mixed aldehyde compounds with retention of the CHO group. Each of these subsections contains an excellent discussion of the general method and is illustrated with numerous specific laboratory syntheses. The significant literature has been reviewed up to the latter part of 1953. Workers who are engaged in any phase of aldehyde chemistry will find this volume very helpful indeed.

The second section of this work (100 pages) deals with the transformation of aldehydes into a great variety of derivatives that are of significant value in the identification, purification, replacement, or protection of the CHO group. The treatment of the subject is very systematic: examples of the reactions, preparation of reagents, splitting of the products, etc., are described in an unambiguous manner. The volume concludes with a short statement on the production of optically active aldehydes and isotopic modifications. The index refers to approximately 2500 compounds.

"Die Methoden der organischen Chemie" is truly one of the most significant reference works in organic chemistry that has appeared in recent years.

GEORGE HOLMES RICHTER

THE RICE INSTITUTE
HOUSTON, TEXAS

● ORGANIC PEROXIDES: THEIR CHEMISTRY, DECOMPOSITION, AND ROLE IN POLYMERIZATION

Arthur V. Tobolsky, **Princeton University, and** ***Robert B. Mesrobian,*** **Polymer Research Institute, Polytechnic Institute of Brooklyn. Interscience Publishers, Inc., New York, 1954. x + 197 pp. 15 × 24 cm. $5.75.**

ORGANIC peroxides, as sources of free radicals, play an important role in polymerization, oxidation, and halogenation reactions. The authors of this book, who have contributed a great deal of original research in this field, have filled an urgent need in compiling all available information on this interesting class of compounds.

The volume is divided into three parts, as indicated in the subtitle. Peroxide-induced polymerization is treated in great detail, and it is perhaps a pity that no similar exhaustive discussion of the other reactions induced by peroxides was included.

A number of valuable tables are included, summarizing kinetic data on polymerization initiated by a variety of peroxides, physical constants of organic peroxides, conditions of their safe handling, and their commercial availability.

HERBERT MORAWETZ

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK

● AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY. VOLUME 4: PHYSICO-CHEMICAL OPTICS

J. R. Partington, **Emeritus Professor of Chemistry, University of London. Longmans, Green and Co., Inc., New York, 1953. xl + 688 pp. Illustrated. 16 × 25.5 cm. $15.50.**

THIS book is the fourth volume of a well-known series. It is in the same style as the preceding volumes on "Fundamental Principles and the Properties of Gases," "The Properties of Liquids," and "The Properties of Solids," and is in seven parts, as follows: *A*, the Refraction of Light (100 pages); *B*, The Polarization of Light (189 pages); *C*, Optical Activity (101 pages); *D*, The Electromagnetic Theory of Light (201 pages); *E*, Magnetic Rotation (40 pages); *F*, Piezoelectricity and Pyroelectricity (6 pages); and Appendix (39 pages).

The treatment is encyclopedic on those subjects that are treated at all. The basis of selection must be appreciated to understand both the omissions and the usefulness of the book. The book is intended to fill certain gaps in an otherwise moderately well-equipped library. It does not discuss lenses, prisms, mirrors, and the like, which are adequately treated in the usual books on physical optics. Neither does it cover atomic spectra, which have have been covered in Volume 1 of this series, nor molecular and Raman spectra, which will be covered in Volume 5. It is confined to visible light, although much of the treatment is more general.

Dispersion may serve to illustrate the treatment. It is introduced and defined on page 3 in the six-page introductory section on refractive index, and appears implicitly throughout the subsequent discussions of refractivity and structure. It is then treated in detail historically, starting on page 78. There are eight pages and some 200 references on Dispersion Equations from Cauchy to Sellmeier, in which the development of the ideas and their embodiment in suitable equations are outlined. The dispersion equations of Sellmeier, Ketteler, and Helmholtz are then discussed in seven pages with some 150 more references. This treatment concludes with short discussions (five pages) of anomalous dispersion, some numerical dispersion results, and dispersion and chemical composition.

Dispersion is again taken up under the electromagnetic theory of light, starting on page 513. Twenty-five pages (in two separate sections) and some 400 references complete the treatment. The discussion of results of the modern quantum theory of dispersion is limited to a little more than a page, introduced by the statement, "It [this theory] is mathematically too difficult to allow of adequate treatment here."

This treatment of dispersion, with its virtues and its defects, is typical. The 189 pages on The Polarization of Light include four on polarizing apparatus, and at the end of these four is one paragraph on Polaroid, concluding with the sentence, "It is supposed that the eye of a bee detects polarized light, which guides the insect in flight." The treatment of light-scattering by particles small compared to the wave length is satisfactorily complete, but that of scattering by larger particles, on which so much research is now going on, is inadequate. Throughout the book in general the interrelations among the earlier theories, their successes and failures, the reasons for and the results of particular postulates are all clearly displayed, but the viewpoint is that of some years ago.

Such a treatment is interesting and valuable for many classes of readers, but not for all who might expect to find help. The student who has occasion to read the early papers or who encounters an unfamiliar equation in such compilations as the "International Critical Tables" will find background and explanation. The scholar concerned with the history of ideas and techniques in theoretical physics will find a clear outline of this history for the topics covered. The experimentalist who merely wishes to select an appropriate equation for use as a laboratory tool may become lost in the details, but enough critical comments are included to guide his decision if he persists. The person who is concerned with research on such a subject as dispersion itself, however, will receive relatively little help, for the discussion does not adequately cover those present-day problems on which research is now proceeding.

CARSTEN STEFFENS

STANFORD RESEARCH INSTITUTE
STANFORD, CALIFORNIA

● CATALYSIS. VOLUME I: FUNDAMENTAL PRINCIPLES, PART I

Edited by ***Paul H. Emmett.*** **Reinhold Publishing Corp., New York, 1954. vi + 394 pp. 15.5 × 23.5 cm. Illustrated. $10.**

THIS text is the first of a series dealing comprehensively with catalysis and is edited by Paul H. Emmett, who is widely known for his researches and contributions in the catalytic field. He has written a chapter on methods of measurement of the surface area of solid catalysts and other solids in which various methods and their applications are presented and critically discussed. The chapter on physical adsorption, which is written by Herman E. Ries, Jr., deals briefly with the classical work and also with the more recent developments in this field. Three chapters, comprising nearly half of the book, are written by Keith J. Laidler. In his first chapter, experimental evidence, mechanisms, and

theories for chemisorption are presented. His second chapter is devoted to a very complete presentation of the kinetic laws in surface catalysis, including a discussion of numerous specific reactions. In these two chapters considerable data are presented in table form. In his last chapter the theory of absolute rates of surface reactions is developed and compared with experiment in several instances. Catalyst carriers, promoters, accelerators, poisons, and inhibitors are discussed in Chapter 6, by W. B. Innes, with the aid of several cuts and the liberal use of tables. In the following chapter F. G. Ciapetta and C. J. Plank discuss techniques of preparation for important metal and compound catalysts. The last chapter, which is devoted to the increasingly important subject of magnetism and catalysis, is written by P. W. Selwood, who deals briefly with theories of magnetism, applications of magnetism to catalysis, and some experimental methods. The book is well printed, contains a very complete set of references to the literature, has author and subject indexes, and has very few typographical errors. The editor and the contributing authors have cooperated most effectively to make the present volume an outstanding contribution to the field of heterogeneous catalysis. This text is a book which everyone having an interest in catalysis will want to own. Because of the uniform excellence of this first volume, the remaining volumes in this series will be awaited with keen interest.

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND
W. W. RUSSELL

● REFRACTORY HARD METALS

Paul Schwarzkopf and *Richard Kieffer,* in collaboration with *Werner Leszynski* and *Fritz Benesovsky.* The Macmillan Company, New York, 1953. xi + 447 pp. 100 tables. 97 figs. 16 × 24 cm. $10.

IN RECENT years, metallurgical workers have developed research in two independent regions of temperature. One searches the region of low temperatures, the approach to absolute zero, and minimum energy levels of materials. Because of its association with modern theoretical physics, this investigation has been widely publicized and its results considered particularly dramatic. The other area of research is that of high temperatures. Because of the inherent difficulties in handling and testing of materials at high temperatures, dramatic results have not been as forthcoming as from the probe into the cold. None the less, there is a continually increasing demand for materials to be used in high temperature applications. In response to this demand, Drs. Paul Schwarzkopf and Richard Kieffer have collaborated with Drs. Werner Leszynski and Fritz Benesovsky to make available to the English-reading scientific world, "Refractory Hard Metals."

In this book the authors offer a summary of an extensive review of the literature on the materials constituting the class of refractory hard metals. The hard metals discussed are limited by the authors to the carbides, nitrides, borides, and silicides of the elements in the fourth through the sixth transition groups and the actinide series. The review and summary have been restricted to an unevaluated presentation of reported information on the structure, preparation, and properties of the above class of materials. The authors cover about 2000 references and have organized the subject matter in a form that will be valuable to the investigators looking for specific information or sources of information on these materials. The information is presented by chemical grouping and subgrouping of nonmetallic and metallic constituents, respectively. The discussions of structure, preparation, and properties are presented under each member of a subgroup. The authors have presented the data of the investigators. It is to be regretted that the authors, with their wealth of experience in this field, did not see fit to evaluate the variant views. It is especially to be regretted that even when the authors are reporting their own variant information, no explanatory comments are provided.

A serious shortcoming of the survey is the absence of any consideration of testing methods and techniques. Testing of more common materials for routine applications has become standardized. Testing of these uncommon materials fabricated for utilization in frontier applications is by no means standardized or well known. As a matter of fact, the absence of satisfactory test methods is a significant handicap to the more rapid development and expanded utilization of these materials. Surely a discussion of current testing techniques, their limits and reliability should be included in a revised edition of this review.

B. BOVARNICK
BRIGHTON, MASSACHUSETTS

● BIOLOGICAL EFFECTS OF EXTERNAL RADIATION

Edited by *Henry A. Blair,* University of Rochester School of Medicine and Dentistry. McGraw-Hill Book Co., Inc., New York, 1954. xvii + 508 pp. Illustrated. 16 × 23.5 cm. $7.

BY FORTUNATE coincidence or perhaps intent, this volume on "Biological Effects of External Radiation" has been released by the publisher almost concurrently with Volume 22B of Division IV of the National Nuclear Energy Series entitled "Biological Effects of External X and Gamma Radiation." Both volumes cover much of the same field but the presentations of the material, methods, and techniques are sufficiently different to be refreshing and make interesting comparative reading.

This book, like many in the National Nuclear Energy Series, loses some of its effectiveness by its late appearance and by the fact that all of the work reported in it was completed by 1947. In spite of this tardiness, which tends to relegate the book to the realm of historical reference, it is so well organized and edited that it is highly worth while reading.

There are two outstanding chapters on an aspect of the effect of external radiation which has received scanty attention previously. These chapters present some very interesting findings on changes in "finger ridge" detail following radiation to the fingers, such as might be encountered in fluoroscope operators, dental X-ray technicians, etc. The chapter covering the cross-circulation experiments by Lawrence and Valentine is well presented, excellently documented, and well worth reading. The idea of dividing the book into three parts is good, and makes for easier understanding of the material presented. The first part covers the methodology as well as growth, pathological, and hematological studies performed after single doses of whole-body radiation, the second part covers similar studies after chronic radiation, while the third part is given over to methodology and pathological studies following fractionated doses of fast neutrons. The third part of the book is primarily of interest because of its historical reference value. The work described in this part is among the earliest biological studies in this field, when methods of measurement were poor and standards of comparison were lacking, so that its value as an active reference is questionable. For a person interested in basic methods of biological study in the field of radiobiology, this book is highly recommended.

FRED A. BRYAN
UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

● MONOMERIC ACRYLIC ESTERS

E. H. Riddle, Rohm & Haas Company, Philadelphia. Reinhold Publishing Corp., New York, 1954. vii + 221 pp. 35 tables. 16 × 23.5 cm. $5.

A TECHNICAL monograph on a subject which the author obviously knows something about. He should, being a prominent member of the staff of one of the principal manufacturers of methacrylates, Rohm and Haas Company.

Out of the Editor's Basket

Viscosimeter Bath

The Sargent S-67428 Viscosimeter bath incorporates the Model SV Thermonitor for detecting and controlling the temperature of the bath. It is recommended for use with Ostwald viscosimeters in accordance with ASTM method D-445 and provides reliable temperature control from a few degrees above temperature of the cooling coil to 212° F. The use of the S-67429 bath, employing an extra deep jar is recommended if Ubbelohde viscosimeters are employed.

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New Universal Clamp

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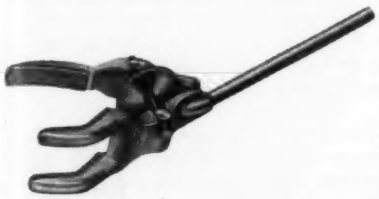

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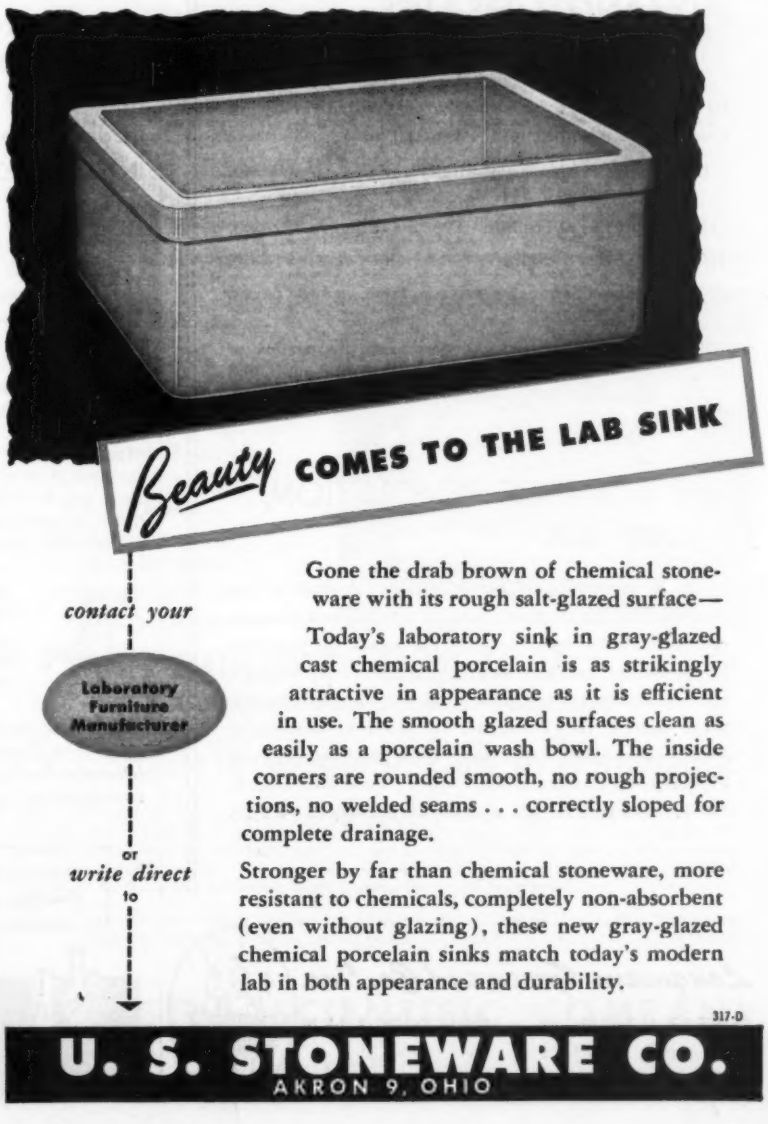
Further particulars may be obtained from Mr. Paul D. Grindle of the Ealing Corp., Box 51 Stuyvesant Station, New York 9, N. Y.

Improved Demonstration of the Cartesian Diver

Ernst M. Goldstein, of Elizabeth, New Jersey, sends us this item.

The principle of the unchanged transmission of pressure by liquids confined within a given volume, the principle of Archimedes, and the compressibility of gases are often illustrated on the lecture table by the Cartesian diver. A bottle is filled with water and after inserting the balanced floats it is covered with a rubber diaphragm which is tightened with string. Assembling or disassembling of this device is tedious and often the seal of the bottle is not tight. A better way to demonstrate the Cartesian diver, allowing also more and finer pressure regulation, is the following: A wide-mouth bottle is filled with water, and the floats, which can be also overbalanced, put in. The bottle is closed with a rubber stopper having a hole in the center. In this hole is now inserted a snugly fitting plug of a stopcock. By lifting or pressing down the rubber stopper a considerable change in pressure in the bottle can be accomplished, resulting eventually in a suitable balancing of the floats. The plug is moved up or down for finer pressure changes, to let the now balanced floats go down or up. These floats are usually in the form of "divers" or "devils."

As it is interesting to observe the in-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CHEMICAL THERMODYNAMICS

By I. Prigogine and R. Defay, both of the University of Brussels. Translated by D. H. Everett, University of Bristol, from the Second Edition (1950) revised in collaboration with the authors. Covers methods developed by the Brussels school of de Donder, based on the work of Gibbs. (The first of three volumes of the set, *Treatise on Thermodynamics;* the second and third volumes are in preparation.) Published Dec. 15, 1954. 543 pages. 6½ by 9½ in. 152 figures. 40 tables. $12.50.

ADVANCED TREATISE ON PHYSICAL CHEMISTRY

By J. R. Partington, formerly of the University of London. In five volumes; 6½ by 10 in.

I. General Properties of Matter and of Gases. 1949. 943 pages. $16.50.

II. Properties of Liquids. 1951. 448 pages. $10.00.

III. Properties of Solids. 1952. 639 pages. $14.00.

IV. Physico-Chemical Optics. 1953. 688 pages. $15.50.

V. Molecular Spectra and Structure, Properties of Dielectrics, Dipole Moments. To be published Jan. 12, 1955. 630 pages. $15.50.

THE SCIENTIFIC REVOLUTION, 1500–1800

By A. R. Hall, Cambridge University. A study of the formation of the modern scientific attitude and method: science in 1500, new currents, the attack on tradition in mechanics and astronomy, experiment in biology, the organization of scientific inquiry in the 1600's, technical factors, the Principate of Newton, descriptive biology and systematics, the origins of chemistry, and experimental physics in the 1700's. Published Dec. 8, 1954. 390 pages. 6¼ by 9 in. Frontispiece. $3.50.

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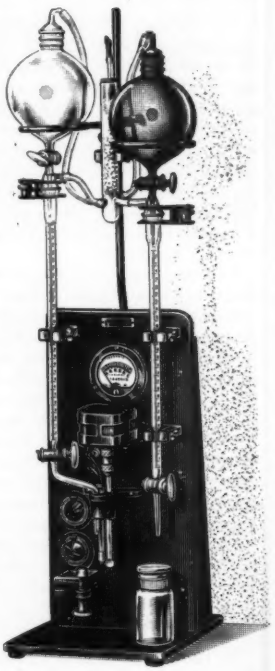

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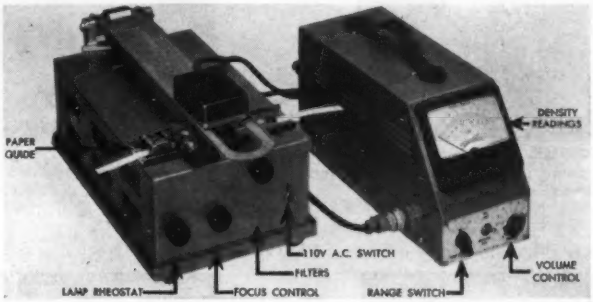

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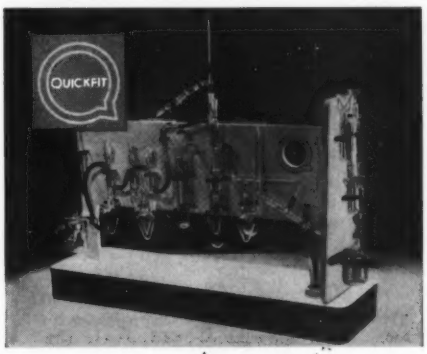

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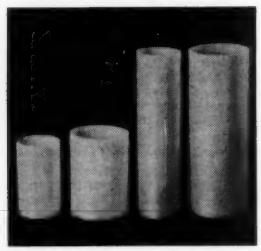
2 gal. . . . . 26.60, 5 gal. . . . . 34.00 each
Prices of 6½- and 13-gal. sizes upon request.



17120T—JARS, Pipette. Resiliency reduces pipette damage. Lightweight, easy to handle even when wet.

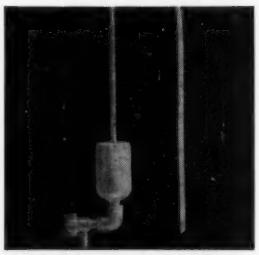
Size A, 5" x 8" . . . . . 9.00 each
Size B, 6½" x 9" . . . . . 10.50 each
Size C, 5" x 18" . . . . . 11.50 each
Size D, 6½" x 18" . . . . . 13.25 each

14150T—FUNNELS, with reinforced rim.

Dia., inches	1½	2½	3½	4½	5½	6½	8½
Price each	.24	.42	.72	1.08	1.50	1.80	2.88
Per doz.	2.40	4.20	7.20	10.80	15.00	18.00	28.80

21005T—PAIL WITH COVER. Lightweight, reinforced construction with tight-fitting cover. Handle attached to *outside* of pail.

11-quart size . . . . . 3.79 each



2070T—SYPHON. To prime merely squeeze bottle. 10.00

Standard and heavy wall beakers, narrow mouth bottles with polyethylene screw caps, graduated cylinders, washing bottles, centrifuge tubes, tubing, wide mouth jars, and pipette jar racks also available. Complete brochure and list of common reagents and how they affect polyethylene at 70°F and 140°F are yours for the asking. Prompt delivery from your nearest WILL office-warehouse listed below.

Will CORPORATION
and subsidiaries

Specialists in WILL *Scientific Supply*

ROCHESTER 3, N.Y. • ATLANTA 1, GA. • NEW YORK 12, N.Y. • BALTIMORE 24, MD. • BUFFALO 5, N.Y.

Greiner Co. Needle Valve Burets in all sizes from macro to micro, it is now possible to control liquids for very fine micro measurements. These new instruments, now available in a great range of sizes, perform titrations without the annoyance of stopcock adjustments.

For complete range of sizes and price list write The Emil Greiner Co., 20–26 N. Moore St., New York 13, New York.

Electronic Relay Control Box

Precision Scientific Company has redesigned its Electronic Relay Control Box to provide a better means of handling substantial power loads with very minute currents over the contacts of regulating devices.

The redesigned Control Box features: high sensitivity—response is assured with a current of as low as 2 micro-amperes; a large power load—up to 15 amperes; four plug-in receptacles—one for continuous power, two for intermittent power, and one for a regulating device; operation on line current of 115/230 volts, 50/60 cycles, normally open or normally closed. Precision Scientific Company, 3737 W. Cortland Street, Chicago 47, Illinois.

New Literature

● Coleman Instruments, Inc., Dept. JCE, Maywood, Illinois, has available an excellent new catalog "Tools for Science" in which the characteristics and merits are given for their Spectrophotometer, Photometer, Colorimeter, Photo-Nephelometer, Nepho-Colorimeter, pH Electrometers and Autotrator. For clarification and easy reference the instrument descriptions are grouped in accordance with the analytical systems to which they are applied. More important, brief discussions of the principles underlying each of the analytical systems is given as well as a good bibliography of more complete information sources.

● A storage cabinet for keeping glass tubing clean, dust-free, and accessible has just been developed by the Bethlehem Apparatus Company, Inc., Hellertown, Pennsylvania. They will gladly furnish information on this piece of apparatus, ask for folder SC-54.

● The Nalge Co., 625 Goodman Street, Rochester 20, New York, has a very comprehensive polyethylene catalog, A954, available on request.

● A new eight page brochure issued by Drage Products, Inc., 406 32nd Street, Union City, New Jersey illustrates the application of a new Swiss-made Viscometer to both laboratory and in-plant process and quality control.

Models "Viscostructure" and "Viscotemp" are claimed by the maker as being designed not only to give specific values for Rheological characteristics such as thixotropy, dilatancy and yield value but of far greater importance, it is specifically designed to accurately detect the relationship of time and temperature to these flow-properties, which are directly responsible for quality.

These instruments operate under extremes of pressure and temperature at shear rates up to 600 sec^{-1}. Shear rates

(Continued on page 40)

Kodak reports to laboratories on:

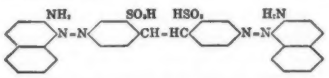
a disazostilbeneaminodisulfonate for precision titrimetry... telling your story without jump or jerk... a new material for the base of our business

Waterman's find

This is how come *4,4′-Bis(2-amino-1-naphthylazo)-2,2′-stilbenedisulfonic Acid Disodium Salt* became Eastman Organic Chemical No. 7000.

We had run across several papers by a chemist in the water supply department of a large city who was bothered by the shortcomings of a certain tool of his trade, namely the indicator methyl orange. This has a rather weak color change which occurs perceptibly only at pH 4.6 and is therefore no good for alkalinities below 150 ppm in acid-carbonate titration. In the interests of precision titrimetry, he had felt, it is better to have a pH indicator change from a light color to a dark color as an end-point is reached, instead of the other way around. In the disazostilbeneaminodisulfonates he found what he was looking for. A number of dyes of this series gave useful color responses in the broad pH range between 8 and 4. Among the several dyes investigated in this class was an obscure item known to dye men as Hessian Purple N Extra, or more simply, Direct Purple.

Whether he tried to buy it out of a dye catalog and failed, he doesn't say. At any rate, he made some by tetraazotizing *4,4′-Diaminostilbene-2,2′-disulfonic Acid* (Eastman T 4613) and coupling with *2-Naphthylamine* (Eastman 174) to get his indicator:

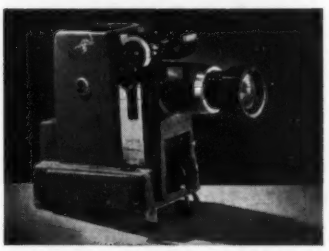


This starts from a deep red, shows a first transition at pH 4.0 to a faint mauve, turns emphatically purple at pH 3.8—a long sight more emphatically than methyl orange ever did—and finally goes over to a bluish purple at pH 3.0. Such behavior is reported a lot more useful for the acid titration of sodium carbonate than even that of our *Methyl Orange-Xylene Cyanole Solution* (Eastman A 2216), which was developed back in 1922. We saw our duty clearly before us to spare analysts from doing their own tetraazotizing and coupling. Thus Eastman 7000. It's used as a 0.1% solution.

Is Eastman 7000 *of special importance to us? No more so than the rest of the some 3500 organic chemicals we stock. They're all cataloged in our List No. 39 which you may have by writing to Distillation Products Industries, Eastman Organic Chemicals Department, Rochester 3, N. Y. (Division of Eastman Kodak Company).*

Talking with film

There is a man in your trading area who calls himself an audio-visual dealer. This mid-20th-century addition to the roster of trades is a merchant of various devices for captivating a captive audience into granting access for your message to their minds through their eyes and ears. Assuming you have a message—most successful people nowadays have one—we point here to a new



and advanced example of one of the basic devices which your audio-visual man has for conveying it, the *Kodaslide Signet 500 Projector, Filmstrip Model.*

First we ask you to grant that the smoother the mechanical aspects of your presentation, the less likely it is to distract your audience from your subject matter. Therefore we have proceeded on the assumption that the pictures should follow each other instantaneously, quietly, positively, without jumping, without jerking. Instead of holding a lot of engineering conferences on how to accomplish this without resorting to a costly Geneva movement, we went ahead and actually used the Geneva movement and then made the engineers figure out how they could still keep the selling price down to $98.

And, since the customers were to be asked to lay their dough out for a projector, not just a Geneva movement, we had to insist on 1) sufficient brilliance and evenness of illumination to dispense with room darkening in most cases; 2) safeguarding the filmstrip by automatic separation of the glass pressure plates before it can move; 3) fast setup by virtue of drop-in loading for immediate sprocket engagement, a quick framing lever, and a quick rewind device; 4) cool operation of a 500-w lamp with little or no blower noise and no danger of burning a hole in the film; 5) automatic leveling capable of compensating for unevenness of support.

All this they did, our engineers, muttering all the while that sales people are unreasonable; for they knew all along that not only were they expected to come up with a world-beater of a filmstrip machine but also that the $98 package had to include a mechanism that the user could easily insert when he had Kodachrome slides to show!

To have the audio-visual man show you how well they fulfilled the assignment, drop a line to Eastman Kodak Company, Department 8-AV, Rochester 4, N. Y. As for how you prepare the filmstrips in the first place, you can ask in your note for a little pamphlet of helpful hints we call "Making Filmstrips With Amateur Equipment."

P(olystyrene) B(ase)

The first Kodak film on a base other than cellulose ester is now on regular sale.

Kodalith Ortho PB Film has a .005″ base of extruded polystyrene. This material is optically clear and as free from visible blemishes as cellulose ester film had become about the time of the Harding administration. What justifies using this material is the fact that when a pelloid is coated on one side and a photographic emulsion on the other, and then you expose it and put it through everything film goes through in processing, drying, and storage, you find it is about three times as dimensionally stable as cellulose ester film. Furthermore, what little dimensional change has occurred is the same in all directions.

Anybody who has been looking for a high-contrast film that probably won't change dimension by more than 0.02% for a 10% change in relative humidity is invited to purchase a box of Kodalith Ortho PB Film *from his Kodak Graphic Arts Dealer.*

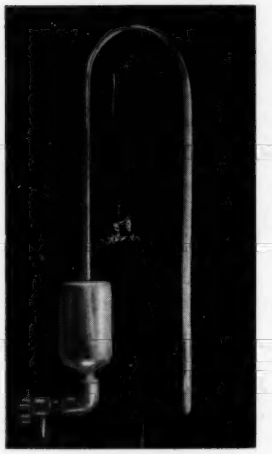
Price quoted is subject to change without notice.

Kodak

This is one of a series of reports on the many products and services with which the Eastman Kodak Company and its divisions are ... *serving laboratories everywhere*

for more efficiency, more economy...

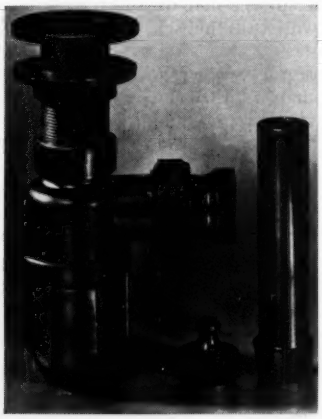
NALGENE* POLYETHYLENE-WARE



NEW! NALGENE* POLY-SYPHON

Constructed completely of Polyethylene; chemical-resistant, safe, simple to use ... merely insert one end in carboy or drum, squeeze flexible bulb to prime, then open spigot to dispense liquid in any quantity desired. Spigot is the well-proven Nalge No. 1292, ½" needle with sufficient tubing for use with 55 gallon drum. Trimming tubing to desired length fits it to smaller units.

NO. 1294 NALGENE* POLY-SYPHON ..... $10.00 each



NALGENE* TRAP-SINK DRAIN

Black Polyethylene which will not break or dent; completely resistant to laboratory chemicals and corrosives; unaffected by the hottest water. Unit consists of trap, outlet union, strainer, lock-nut, stopper and stand-up pipe. May be connected either to threaded parts or to unthreaded pipe through a special flexible joint not shown here. Simple to remove, clean, and assemble without tools.

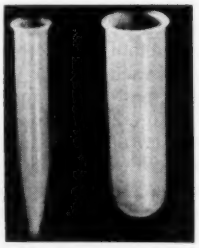
NO. 1288 COMPLETE UNIT without stand-up pipe $25.50 each
NO 1288A STAND-UP PIPE FOR ABOVE, 7" TALL . $ 2.85 each

NEW! 5 GAL. SIZE NALGENE* CARBOY

The new 5 Gal. size is added by popular demand to our regular line of 2, 6½, and 13 Gal. Nalgene* Polyethylene Carboys. All are blow-molded in single piece; light, unbreakable, chemical-resistant, and fitted with our standard 83mm screw cap. New 5 Gal. size available also in aspirator type fitted with the well-known ½" needle type Nalgene* Polyethylene spigot.

NO. 1204-1 5 Gal. NALGENE* POLYETHYLENE CARBOY ..$12.75 each
NO. 1208 ASPIRATOR TYPE WITH ½" SPIGOT .....$28.00 each

NALGENE* CENTRIFUGE TUBES
NEW 100 ML SIZE
NEW LOW PRICES



NO. 1210 NALGENE CENTRIFUGE TUBES

15 ML capacity, conical type .30 each.; 50 ML capacity, round bottom .40 ea.; 100 ML capacity, round bottom 1.10 ea.

DISCOUNTS: Package lots of 36 of a kind, less 10%. Lots of 144 assorted but not less than 36 of a kind, less 15%.

Nalgene* Centrifuge tubes are automatic-machine molded from high molecular weight polyethylene; clean, resilient, acid and alkali resistant and completely guaranteed to withstand the greatest centrifugal force currently employed. Ever-increasing demand permits these new low prices.

*NALGENE is the trademark for NALGE POLYETHYLENE-WARE

Write for
NALGENE
Catalog No. A954

The NALGE CO., Inc.
Rochester 2, New York

(*Continued from page 38*)

petroleum and its products, such as gravity, color, viscosity, distillation range, vapor pressure, gum content, sulfur, carbon residue, flash point, water and sediment, melting point, cloud and pour points, and consistency.

● The latest information on properties and applications of Bakelite vinyl butyral resins is compiled in a new technical booklet issued by Bakelite Company. Widely known for their part in making safety glass possible, these resins are growing rapidly in use as wash primers or metal conditioners, wood and metal finishes, adhesives and cloth coatings. Numerous graphs and tables based on recent laboratory data are included in the 27-page booklet. Five basic types of wash primer, or metal conditioner, are described in detail. Copies of this booklet, "Bakelite Vinyl Butyral Resins, Technical Release No. 11," can be obtained from Bakelite Company, a Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, N. Y.

● For the benefit of young people planning careers, America's fifth largest industry is described and job-classified in "A Guide to Career Opportunities in the Paper Industry," an 80-page monograph.

Paper's vital role in the American economy is discussed in Part I, with particular emphasis on the opportunities for young people who will be tomorrow's leaders in executive, administrative, engineering, and scientific positions.

One section of the pamphlet is devoted entirely to job descriptions. Readers can relate the needs of various jobs to their own scholastic activities and thus plan their studies accordingly. This material is for the guidance of students who plan to complete college, university, or technical education.

Free copies of "A Guide to Career Opportunities in the Paper Industry" can be obtained from the American Paper and Pulp Association, 122 East 42nd Street, New York 17, N. Y.

● All the products commercially available from Synthetics Department, Hercules Powder Company, are conveniently listed, with characterizing data, in a new technical booklet. The booklet includes listing of synthetic resins, plasticizers pentaerythritol, and nonionic surface-active agents. Certain key properties of the products are included in the listings. Applications for the synthetic resins, which vary from liquids to high-melting solids, include protective coatings, inks, plastics, wood-treating chemicals, chewing gum, floor coverings, and adhesives. Plasticizers for nitrocellulose, polyvinyl chloride, vinyl chloride-acetate copolymers, and polyvinyl acetate; and nonionic surface-active agents useful as detergents, emulsifiers, and aids in textile processing and petroleum production are covered.

● Eastman Kodak Company has just published a folder illustrating and describing its new Kodagraph Microprint Reader, a device designed to be used in offices and libraries where literature and reference books have been reduced to microprint cards. Copies of the folder, titled "The Kodagraph Microprint Reader, Model A" may be obtained on request to Eastman Kodak Company, Rochester 4, New York.

A New International Centrifuge

FOR THE Modern Laboratory

The new INTERNATIONAL MODEL U is more than just a Centrifuge in a cabinet. International's experienced engineering has produced a Centrifuge with years-ahead features and unmatched performance.

You will want to know more about the new aerodynamic guard bowl ventilating system—the new stainless steel interior — the stainless steel auxiliary cover that saves valuable bench space — the electric tachometer — the electric time clock — the unique air-filtering system—the spring-loaded hinge — the new vibration dampening system which results in smooth operation without the "shaker" action of over-flexible mountings — the versatility of 84 interchangeable accessory combinations.

Let us tell you more about this completely new Centrifuge, handsomely designed to fit in with your wall counters and cabinets. Write for Bulletin J explaining all these features in detail.

INTERNATIONAL EQUIPMENT COMPANY

1284 SOLDIERS FIELD ROAD, BOSTON 35, MASS.

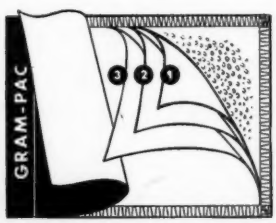
the Fisher
GRAM-PAC

First major improvement in reagent packaging in years

This completely sealed, tough, laminated package eliminates the traditional (and expensive) quarter-pound bottle. It eliminates overlapping sizes, cuts ordering costs, reduces shipping costs and there is no breakage to contend with.

GRAM-PAC permits the packaging of "individual" amounts of reagents for easier distribution and greater laboratory convenience. They are packed 10 PACS to a box and 12 boxes to a case. Eventually, all Fisher Certified Reagents will be available in the inexpensive, contaminant-free GRAM-PAC, including the nearly 200 chemicals specified by the American Chemical Society.

Another "first" from the Fisher Chemical Manufacturing Division . . . to make life easier . . . for you.



WHAT IS GRAM-PAC?

1. **POLYETHYLENE,** next to reagent, for chemical inertness
2. **ALUMINUM FOIL,** for strength and insulation
3. **ACETATE,** for waterproofing

FREE SAMPLE-a GRAM-PAC of Fisher Certified Reagent Sodium Hydroxide, ACS, is waiting for you. Write today to Fisher Scientific, 717 Forbes St., Pittsburgh 19, Pa., ask for "Sample GP-16"

FISHER SCIENTIFIC

Boston	Cleveland	Philadelphia	Washington
Buffalo	Detroit	Pittsburgh	Montreal
Chicago	New York	St. Louis	Toronto

America's Largest Manufacturer-Distributor of Laboratory Appliances and Reagent Chemicals